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Editorial

Inflation vs. The Decennial Index

WHEN HENRY DAVID THOREAU, famous Concord naturalist and Yankee philosopher, traveled to Canada one fall day in 1850, prices were low. How low can be judged by the fact that his railroad fare to Quebec City and return was seven dollars. His food, lodging, and incidentals cost another five dollars. On the other hand, a laborer in his time earned a straight one dollar a day, which was frequently what Thoreau was paid when he was hired to do odd jobs for his neighbors. Compared with conditions now, the present workman, receiving ten to twenty dollars a day plus deluxe fringe benefits, is undoubtedly better off even though the railroad fare from Concord to Quebec has increased $4\frac{1}{2}$ times. Prices have gone up but so have wages.

The situation admittedly is not so favorable with white collar workers, and with fixed income groups. A man earning $3000 a year, only ten years ago, apparently must now earn $5500 to achieve equal purchasing power. If he earned $5000 in 1940 this is now equivalent to $9400. Families with fixed income derived from pensions and life insurance payments have in part lost the security they once thought they had by a factor of approximately one half.

Technical societies also find the going rather rough. Although our dues have gone up 20% in the past 20 years, prices and wages paid by the Society have gone up many times this amount. (Incidentally, officers of the Society continue to serve without pay.) Economy and more economy is necessary to make ends meet. This year, for the first time, the Decennial Index for the TRANSACTIONS and JOURNAL will be omitted. Why? The budget does not permit. The Board of Directors feels that the Index is less important to the membership than full support of the JOURNAL at present publication standards. Only sizable subsidies from outside sources can make the Index possible without cutting into essential operations and services of the Society at their current levels. Approaching such time as the inflationary flood recedes, or the Society's income catches up, the Index will again be made available.

In a period of austerity, postponement of this kind constitutes a small sacrifice on our part; and one which should not seriously hamper the national mobilization effort. On a broad front, the Society continues to serve on a scale higher than at any other time in its history.

How to Dispose of Waste Cyanide Solutions

A DISPOSAL METHOD now coming into wide use is that of oxidizing the cyanide ion to the much less toxic cyanate in a strongly alkaline solution.

CYANATES are about $\frac{1}{1000}$ as toxic as *cyanides*. Accordingly, waste containing 100 ppm cyanide becomes practically non-toxic if the cyanide is all oxidized to cyanate.

THE OXIDATION OF CYANIDE to cyanate is not only rapid, but it appears applicable to almost all types of cyanide wastes.

MANY OXIDIZING AGENTS can be used, but chlorine is probably the most satisfactory and cheapest. It may be fed as a gas, an aqueous solution, or as solid hypochlorite.

FORTUNATELY, after a basic solution of cyanide is oxidized to cyanate, the further addition of chlorine decomposes it to carbon dioxide and probably nitrogen or nitrogen compounds.

PUBLIC SEWERS are generally used as outlets for waste from plants that are not located on streams. Usually, higher concentrations are permissible than in streams, although local conditions and legal requirements dictate allowable practice. Actually, even though cyanates are not particularly poisonous, there is a tendency on the part of pollution control authorities to require destruction of the cyanates.

A.E.S. RESEARCH PROGRAM

THE AMERICAN ELECTROPLATERS' SOCIETY is conducting a comprehensive research program and has developed useful information on current plating problems. International Nickel, in addition to its other support of this program, feels that it will be a further service to make copies of A.E.S. Research Reports available to electroplaters.

THE SUBJECT OF CYANIDE WASTE TREATMENT, approached from different viewpoints, is reviewed in A.E.S. RESEARCH REPORT, Serial No. 14, entitled: "Disposal of Plating Room Wastes." We offer you a free copy of this report. Write for it now.

* * *

On January 1, 1951, National Production Authority Order M-14, respecting the consumption of primary nickel, went into effect and subsequent amendments limit the applications for which nickel and its alloys may be used.

Within these limitations, we shall continue to issue information on new developments and user experience with nickel-containing materials, as we believe that dissemination of such data can help to promote the intelligent utilization of critical materials, so essential in these times.

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Electrochemical Reduction of Nitroalkanes

Preparation of *N*-Alkylhydroxylamines (Hydroxaminoalkanes)[1]

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ABSTRACT

Electrochemical reduction of the nitroalkanes gives *N*-alkylhydroxylamines and alkylamines, the former being formed in the larger amounts and in satisfactory yields. The effects of current density, temperature, and acidity on the efficiency of the electrochemical reduction were studied and the optimum conditions for the several reactions were established. Nitromethane, 1-nitropropane, and 2-nitropropane were reduced and the corresponding alkylhydroxylamines and alkylamines were identified as the products of the reactions. The cathode potentials for the several electrochemical systems were measured at different current densities. In order to extend the applicability of the procedure, a nitroalcohol was reduced to a hydroxaminoalcohol.

INTRODUCTION

The nitroalkanes, which have become available in large quantities in recent years, have made possible the initiation of many important investigations. *N*-Alkylhydroxylamines (hydroxaminoalkanes) have been merely laboratory curiosities and only a few studies on these substances have been reported. Pierron (6) has demonstrated that the nitroalkanes, nitromethane, nitroethane, and 1-nitropropane could be reduced electrochemically to the corresponding *N*-alkylhydroxylamines and alkylamines. The cathode was a nickel cylinder, the anode either platinum or nickel. The catholyte was 1.5 per cent sulfuric acid in 50 per cent aqueous alcohol, and the anolyte was 15–20 per cent aqueous sulfuric acid. Current densities varied from 0.4 to 0.75 amp/dm^2. Bruckner and co-workers (2, 9, 10, 11) have effected the electrochemical reduction of aromatic substituted nitroalkanes and derivatives using a mixture of glacial acetic acid, ethanol, and hydrochloric acid as catholyte and 20 per cent sulfuric acid as anolyte. Petru (12) made a polarographic study of the reduction of the simple nitroparaffins. McMillan (13) patented a process involving the reduction of nitroalcohols to aminoalcohols in a 10 to 25 per cent solution in a catholyte containing 1 to 10 per cent hydrochloric acid at 50° to 100°C at a current density of 20 amp/dm^2. Pearson and Evans (5) demonstrated the formation of *N*-alkylhydroxylamines among the products of the electrolysis of pure nitroalkanes with platinum electrodes.

The purpose of the investigation described in the present paper was to establish the optimum electrochemical conditions for the reduction of nitroalkanes to *N*-alkylhydroxylamines.

EXPERIMENTAL PROCEDURES

Apparatus.—The cell employed gave essentially the same electrochemical conditions as that developed by Skolnik and Smith (7) for the preparation of aminoguanidine from nitroguanidine. The exact arrangement was as follows: An 8-liter pyrex glass rectangular battery jar served as the container; a small lead shelf in the bottom of the jar supported two rectangular porous clay cells which were the anode chambers. The catholyte was agitated either by the small laboratory pump which circulated the liquid through a lead coil cooled in a low temperature bath, whereby any temperature down to 0°C could be maintained, or by a glass stirrer which operated in the free space below the anode chambers. Direct current from a 12 volt, 1.2 kw motor-generator set was distributed to the electrodes by three lead wires to the cathode, and two similar wires to each of the anodes.

The anodes were lead plates. The cathode used in most of the experimental work was an amalgamated lead electrode (10.6 dm^2 surface area) made from lead plate of $\frac{1}{4}$ in. thickness and was of a technical grade only and not a chemically pure (or electrolytic) grade. The lead cathode was cleaned and amalgamated freshly before each experiment. This was accomplished by washing with a mixture of equal volumes of nitric acid and water for several minutes, followed by rinsing with water and then drying with

[1] Manuscript received November 30, 1949. This paper, prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950, is an abstract of a part of the thesis submitted by Morton W. Leeds to the Graduate Faculty of Polytechnic Institute of Brooklyn in June 1944 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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a clean cloth. The electrode was then treated with mercury using a clean cloth to rub the mercury into the surface of the lead electrode until an even mirror-like finish was obtained.

Analytical Methods

N-Alkylhydroxylamines.—Benedict-Fehling's solution containing 18 g/l $CuSO_4 \cdot 5H_2O$ was prepared as outlined by Hawk and Bergeim (3). The preparation was standarized against a solution of alkylhydroxylamine prepared by hydrolyzing a known weight of the *p*-nitrobenzaldehyde derivative of the alkylhydroxylamine. The equations of the reaction which was used in computing the results of the analyses were:

$$R\text{—NHOH} + 2\text{CuO} \rightarrow R\text{NO} + \text{H}_2\text{O} + \text{Cu}_2\text{O}$$

and

$$2R\text{—NHOH} + 4\text{CuO} \rightarrow \text{N}_2\text{O} + 2R\text{OH} + \text{H}_2\text{O} + 2\text{Cu}_2\text{O}.$$

A 10-ml aliquot was withdrawn from the cell and diluted to 100 ml in a volumetric flask. The diluted solution was titrated into 5 ml of the Benedict-Fehling's solution contained in a white porcelain casserole and kept just at the boiling temperature over a small flame. The point at which the blue color had just disappeared was accepted as the end point of the titration.

Alkylamines.—The separation of the alkylamine was effected by oxidizing the *N*-alkylhydroxylamine with ferric ion in acidic solution.

Alkylamines were determined by titration with hydrochloric acid after separation from the catholyte by distillation. *N*-Alkylhydroxylamines which either would distill unchanged along with the alkylamines or would decompose with formation of ammonia, in either case interfering with the titration, must be destroyed before separation of the alkylamines. Accordingly, the following procedure was followed:

Ten cm^3 of catholyte were placed in a 500 cm^3 Kjeldahl flask with 25 cm^3 of 20 per cent ferric sulfate and 5 cm^3 of concentrated H_2SO_4, and the mixture was diluted to 300 cm^3. The diluted solution was boiled vigorously for 15 minutes, then cooled to room temperature. The ferrous ion formed by reaction with the hydroxylamine was restored to the ferric state by addition of sufficient potassium permanganate to cause a permanent pink color. [The reaction of ferric ion and alkylhydroxylamine is quantitative and can be made the basis of a method for determination of alkylhydroxylamines (1)]. Excess alkali was added and the alkylamine was distilled from the solution into 100 cm^3 of one per cent boric acid. Titration was carried out with 0.1*N* HCl, with methyl red as indicator.

Isolation of N-alkylhydroxylamines.—Pierron isolated the alkylhydroxylamines either as *p*-nitrobenzaldoximes or as chloroplatinates which are suitable only for identification. Experiments were performed to see if the sulfate or the hydrochloride of the alkylhydroxylamines gave crystalline products. The sulfate proved to be the most stable, although in no case were we able to isolate pure crystalline solids; but the catholyte solutions could be evaporated under reduced pressure to a thick syrup which could be analyzed for alkylhydroxylamines.

2-Nitropropane was reduced in a 5 per cent solution of sulfuric acid at 5°C using an amalgamated lead cathode. The catholyte was divided at the end of the reduction; part A was treated with an excess of barium carbonate and the barium sulfate removed by filtration. The solution was treated with an excess of hydrochloric acid. Part B was used directly without conversion to chloride, and both solutions were concentrated under reduced pressure at a temperature of 65°C. Part A, or the hydrochloride of the alkylhydroxylamine, gave a yield of only 9.6 per cent while part B, or the sulfate, gave 53 per cent by analysis.

The above experiment was repeated and the catholyte again divided into two portions. To the first portion, A, barium carbonate was added in sufficient amount so that the *N*-alkylhydroxylammonium acid sulfate remained in solution. To the second portion, B, an additional molar quantity of barium carbonate was added so that secondary *N*-alkylhydroyxlammonium sulfate remained. The barium sulfate formed was separated by filtration and the solutions were concentrated under reduced pressure and then further concentrated in vacuum desiccators over concentrated sulfuric acid. No crystals were formed in either case. The yield for part A was 66.6 per cent, and for part B was 65.5 per cent by analysis for isopropylhydroxylamine. The procedure outlined for part B was followed for subsequent experiments in concentrating the catholytic solutions.

Experimental Results

In all of the following experiments nitroparaffin was added to the catholyte at such a rate as to maintain the solution in a saturated condition. The weight of nitroparaffin added was used to calculate the yields.

Effect of variables on the reduction of 2-nitropropane.—2-Nitropropane was selected for the series of experiments designed to establish optimum electrochemical conditions for reduction to the alkylhydroxylamine (2-hydroxaminopropane). The variables studied were current density, temperature, and concentration of sulfuric acid. In the first series of experiments, during which the current density

was varied, a solution of 5 per cent sulfuric acid was used as the catholyte, a lead cathode was employed, and the temperature of 5°C was maintained. The reaction was allowed to proceed for 20 hours and aliquots were withdrawn and analyzed each hour for alkylhydroxylamine and alkylamine. The results of these experiments are presented in Table I.

In a second series of experiments a current density of 1 amp/dm² was maintained and the temperature was changed from 5° to 65°C. Other conditions were as used in the first series. The results of these experiments are presented in Table II.

TABLE I. *Effect of current density on current efficiency in the reduction of 2-nitropropane*
(5% H_2SO_4, 5°C, 20 hr)

Current density amp/dm²	Average current efficiency			Yield 2-hydroxamino-propane, %
	2-hydrox amino-propane, %	2-amino-propane, %	Total, %	
0.5	84.2	3.5	87.7	69.5
1.0	81.5	3.7	85.2	71.5
2.0	71.5	5.3	76.8	65.5
3.0	64.2	7.7	71.9	53.0

TABLE II. *Effect of temperature on current efficiency in the reduction of 2-nitropropane*
(1.0 amp/dm², 5% H_2SO_4, 20 hr)

Temp °C	Average current efficiency			Yield 2-hydroxamino-propane, %
	2-hydrox-amino-propane, %	2-amino-propane, %	Total, %	
5	81.5	3.7	85.2	71.5
25	80.2	2.6	82.8	63.0
45	72.0	3.7	75.7	63.5
65	57.7	8.1	65.8	34.0

TABLE III. *Effect of concentration of sulfuric acid on current efficiency in the reduction of 2-nitropropane*
(1.0 amp/dm², 25°C, 20 hr)

Acidity % sulfuric acid	Average current efficiency			Yield 2-hydroxamino-propane, %
	2-hydrox-amino-propane, %	2-amino-propane, %	Total, %	
0	55.1	18.3	73.4	40.3
1	62.9	20.2	83.1	49.2
3	69.5	3.3	72.8	53.0
5	80.2	2.6	82.8	63.0

In a third series of experiments, the temperature of the catholyte was maintained at 25°C, the current density at 1 amp/dm², and the concentration of sulfuric acid was varied from 0 to 5 per cent. Pierron (6) has shown that at a concentration of 10 per cent sulfuric acid, decomposition of the alkylhydroxylamine results. The data from these experiments are presented in Table III.

Reduction of four nitroalkanes.—From the preceding experiments it appears logical to accept the following as the optimum conditions for the electrochemical reduction to the hydroxaminoalkanes stage; current density, 1 amp/dm²; temperature, 5°C; concentration of sulfuric acid, 5 per cent. Using these conditions, a fourth series of experiments was performed in which the four common nitroalkanes, nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane, were reduced. The current efficiencies and yields for the several compounds are given in Table IV.

For identification purposes, the *p*-nitrobenzaldoximes of the hydroxaminoalkanes were prepared as follows: Approximately 5 g of the concentrated catholyte, obtained as described previously, were diluted with 40 ml of ethyl alcohol. Four g of *p*-nitrobenzaldehyde and 5 g of sodium carbonate were added. The mixture was shaken occasionally for a period of one hour, allowed to stand for 20 hours, and then poured into 150 ml of ice and water. The yellow precipitate was separated by filtration and recrystallized from ethyl alcohol. The melting points and analyses for nitrogen are given in Table V.

TABLE IV. *Current efficiencies for four nitroalkanes*
(1 amp/dm², 5°C, 5% H_2SO_4, 20 hr)

Compound	Average current efficiency			Yield hydrox-amino-alkane, %
	Hydrox-amino-alkane, %	Amino-alkane, %	Total, %	
Nitromethane	60.6	6.9	67.5	41.5
Nitroethane	61.7	5.7	67.4	42.5
1-Nitropropane	71.1	3.3	74.4	54.5
2-Nitropropane	81.5	3.7	85.2	71.5

TABLE V. *Analytical data on hydroxaminoalkane benzaldoxime derivatives*

Derivative	Melting point °C		Nitrogen, %	
	Found	Recorded	Found	Calcd.
Methyl	198	202	15.17	15.55
Ethyl	95	97	15.54	14.50
1-Propyl	74	77	13.22	13.45
2-Propyl	134	138	13.55	13.45

Reduction of a nitroalcohol.—In order to extend the method developed for the reduction of nitroalkanes, a nitroalcohol, 2-nitro-2-methyl-1-propanol, was reduced under the following conditions: current density, 1 amp/dm²; sulfuric acid concentration, 5 per cent; temperature, 30°C; time, 20 hr; amalgamated lead cathode. Concentration of the catholyte, as in the case of the hydroxaminoalkanes, resulted in the decomposition of the product. However, when the sulfate ion was removed as barium

TABLE VI. *Cathode potential as a function of current density in the reduction of the four nitroalkanes*

Current density amp/dm²	Potential across cell, volts	Cathode potential, volts
		Nitromethane
0.5	3.0	0.718, 0.709, 0.710
1.0	3.7	0.733, 0.735, 0.744, 0.764
2.0	4.6	0.772, 0.784, 0.772
3.0	5.7	0.801, 0.802, 0.805
4.0	6.6	0.942, 0.948, 0.950
5.0	7.8	1.910
6.0	8.7	1.221
		Nitroethane
1.0	3.7	0.826, 0.826, 0.829
2.0	4.8	0.886, 0.888, 0.889
3.0	6.1	1.205, 1.175, 1.119
4.0	7.4	1.303
		1-Nitropropane
0.5	3.0	0.670, 0.659, 0.676, 0.679
1.0	3.8	0.730, 0.706, 0.709, 0.721, 0.729
2.0	4.9	0.769, 0.749, 0.726, 0.740, 0.736
3.0	5.8	0.786, 0.757, 0.756, 0.757
4.0	7.0	0.778, 0.763, 0.768
5.0	7.5	0.797, 0.783, 0.780
6.0	8.6	1.105, 1.035, 1.253, 1.313
		2-Nitropropane
0.5	3.5	0.720, 0.714, 0.733, 0.734, 0.731
1.0	4.5	0.764, 0.773, 0.761, 0.763
2.0	5.5	0.785, 0.821, 0.845, 0.810, 0.790, 0.808
3.0	6.5	0.968, 0.929, 0.955, 0.800, 0.843

sulfate, the resulting solution of the hydrochloride was concentrated and a *p*-nitrobenzaldoxime was prepared in the usual manner: mp 161°C; nitrogen analysis—found, 12.13 per cent, calcd., 12.35 per cent; current efficiency was 85.9 per cent, and yield, 28.5 per cent.

Measurements of cathode potential as a function of current density.—Lingane (4) has pointed out that changing the current density to produce a desired rate of electrolysis will also affect the cathode potential. In order to confirm the physical observations made in our previous work, a series of experiments was carried out in which the cathode potential was measured under different conditions of current density. A Leeds & Northrup Type K potentiometer, with a box galvanometer and usual standard cell, was used. A saturated calomel half-cell was fitted with a small section of rubber tubing attached to the side arm; the rubber tubing was in turn attached to a glass tube. The glass tube and rubber tubing were filled with a saturated solution of potassium chloride and the free end of the glass tube was closed with a jelly made from 4 per cent agar-agar in a saturated solution of potassium chloride to prevent diffusion. This arrangement made it possible to move the end of the "extension arm" of the calomel half-cell to any desired position near the surface of the cathode and to obtain readings; the tip of the glass tube had to be in contact with, or not more than 1–2 mm removed from, the surface of the cathode. After the cell had been in operation for at least four hours and control analyses indicated

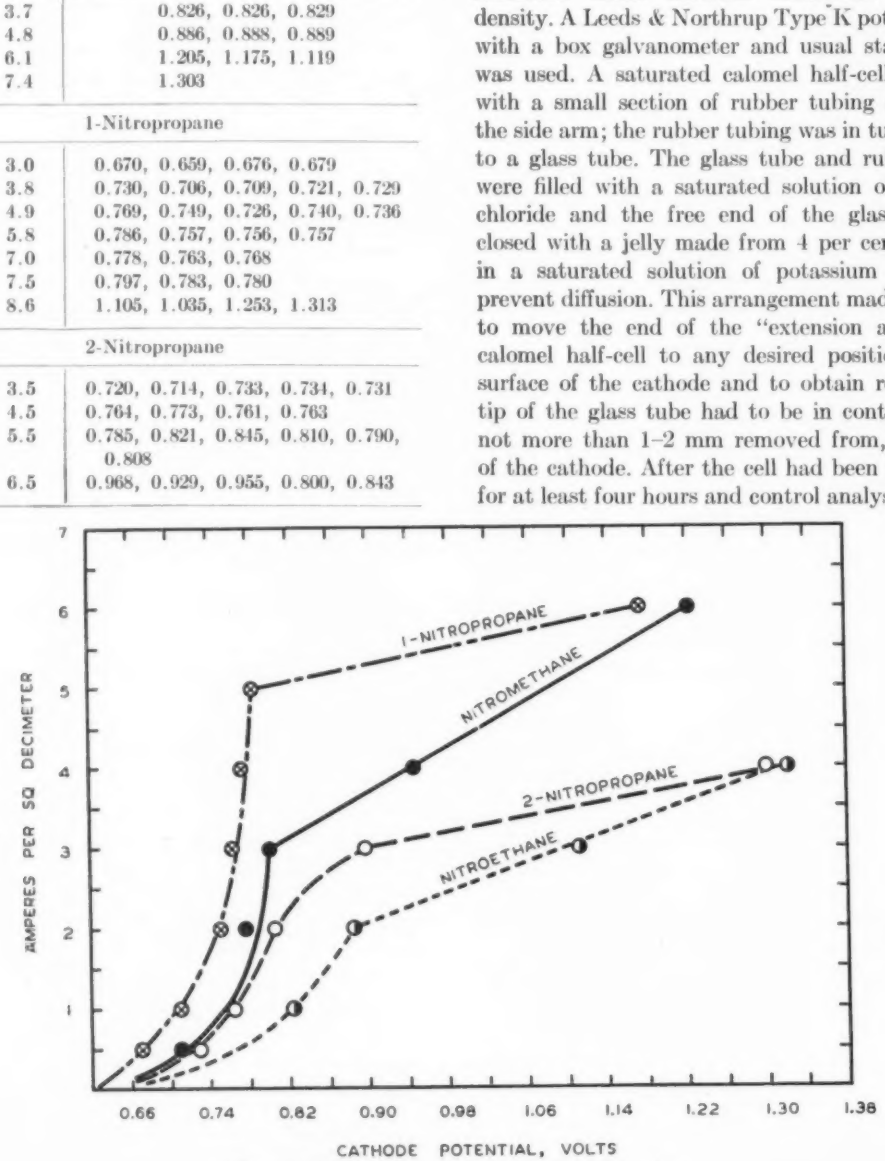

FIG. 1. Cathode potential versus current density

normal functioning, measurements were made. All four nitroalkanes were reduced in 5 per cent solutions of sulfuric acid using amalgamated lead cathodes and temperatures of 25° to 30°C. Since the source of the current was a motor generator, slight current changes occurred, which in turn caused changes in cathode potential. Accordingly, each reading recorded is the average of 3 to 6 measurements and each reading recorded is for one position in the surface of the cathode. The current density was increased until hydrogen was observed to be liberated rapidly from the electrode, indicating that the limiting current density had been passed. Results of these measurements are given in Table VI and Fig. 1.

Discussion of Results

It is evident from the studies described in this paper that nitroalkanes can be reduced to hydroaminoalkanes in an efficient and satisfactory manner by electrochemical means. Rather high current efficiencies have been realized and satisfactory yields have been obtained.

A series of rather empirical experiments established optimum electrochemical conditions for reduction; these findings were supported by analytical data.

Glasstone (8) states that during electrolysis the cathode potential increases until the discharge of another cation, e.g., hydrogen ion, can take place. The limiting current density is the point at which a rapid increase of potential is observed and it represents the limiting (maximum) rate at which the particular ion can be discharged under the given experimental conditions.

Fig. 1 demonstrates that when the cathode potential is plotted against the current density the potential increases slowly as the current density is increased until the point of limiting density is reached. Since all of the electrolytic reductions were carried out at current densities lower than the limiting density values, this may account for the high efficiencies generally obtained.

Summary

Optimum conditions for the electrochemical reduction of 2-nitropropane to 2-hydroxaminopropane using amalgamated lead cathodes and lead-lead oxide anodes have been established. These conditions are as follows: sulfuric acid concentration of catholyte and anolyte, 5 per cent; temperature 5°C; current density, 1 amp/dm^2. These conditions were found by a study of the effect of the several variables on the cathode current efficiency.

Nitromethane, nitroethane, and 1-nitropropane, as well as 2-nitropropane, were reduced and the corresponding hydroxaminoalkanes were identified by preparing the nitrobenzaloximes. The order of increasing current efficiency was nitromethane, nitroethane, 1-nitropropane, 2-nitropropane. The cathode potentials for the reduction of the four nitroalkanes were determined at different current densities. Under optimum conditions, only a small amount of aminoalkanes is formed. A nitroalcohol was reduced to a hydroxaminoalcohol.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the Journal.

REFERENCES

1. W. C. Bray, M. E. Simpson, and A. A. MacKenzie, *J. Am. Chem. Soc.*, **41**, 1363 (1919).
2. V. Bruckner, A. Kramli, and E. Vinkler., *Acta Lit. Sci. Regiae Univ. Hung. Francisco-Josephinae Sect. Chem. Mineral Phys.*, **6**, 145 (1938).
3. P. B. Hawk and O. Bergeim, "Practical Physiological Chemistry," 10th ed., p. 889, P. Blakiston's Sons & Co., Philadelphia, Pa. (1931).
4. J. J. Lingane, C. G. Swain and M. Fields, *J. Am. Chem. Soc.*, **65**, 1348 (1943).
5. R. Pearson and W. V. Evans, *Trans. Electrochem. Soc.*, **84**, 110 (1943).
6. H. Pierron, *Bull. soc. chim. France*, **21**, 780 (1899).
7. S. Skolnik and G. B. L. Smith, Unpublished Notes; See also, G. B. L. Smith, P.B. Report No. 31096 (OSRD No. 138, Serial No. 76).
8. S. Glasstone, "Introduction to Electrochemistry," p. 448, D. Van Nostrand Co., Inc., New York (1942).
9. V. Bruckner and V. Kardos, *Ann.* **518**, 226 (1935).
10. V. Bruckner and A. Kramli, *J. prakt. Chem.*, **143**, 287 (1935).
11. V. Bruckner and A. Kramli, *J. prakt. Chem.*, **148**, 117 (1937).
12. F. Petru, *Collection Czechoslov. Chem. Communs.*, **12**, 620 (1947).
13. G. W. McMillan, U. S. Pat. 2,485,982, October 25, 1949.

Production of Ozone with Refrigerated Anodes[1,2]

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ABSTRACT

By electrolysis of 40 weight per cent perchloric acid with refrigerated platinum metal anodes, electrolytic ozone of 58 weight per cent concentration has been prepared at energy efficiencies up to 24 grams ozone per kwhr. Maximum yields of ozone were attained with the internally cooled anode at −60° to −65°C, perchloric acid electrolyte at a bulk electrolyte temperature of −56°C, current density of 0.13 to 2.6 amp/dm², and a total pressure above the electrolyte of 10–100 mm Hg.

Ozone current efficiency, weight per cent ozone, and grams of ozone per kwhr increase with decreasing anode and electrolyte temperatures, and with increasing current density.

Introduction

Yields of ozone above 20 weight per cent have previously been obtained by electrolysis of perchloric acid at low temperatures (7). A recently completed study demonstrated that the temperatures of platinum metal anodes in perchloric acid are 3° to 20°C warmer than that of the electrolyte, under the optimum conditions for ozone production (1). Since the ozone current efficiency increases very rapidly with decrease in temperature, and since ozone production occurs only at the anode surface, the control of anode temperature is of prime importance. The present work is a continuation and further exploration of that process with the aims of greater yields, higher energy efficiencies, and a better understanding of the process itself.

Briner, *et. al.*, (4, 5) reported that yields of ozone up to 7.8 g/kwhr may be obtained by electrolysis of perchloric acid, and concluded that the acid gives somewhat lower yields than sulfuric acid. Since Briner erroneously believed it necessary to sweep out the ozone with a current of air, he succeeded in obtaining only very dilute concentrations, and since his highest yields were secured with a current of 0.05 ampere, his errors may have been large. In any event Briner and all other prior art workers (3, 6) overlooked the singularly improved results obtainable with perchloric acid.

Experimental Apparatus and Procedure

Cell for Preparation of Hydrogen-Free Ozone

One of several cells having a refrigerated anode is shown in Fig. 1. The cell (henceforth, Cell No. 1) consists of two concentric glass tubes, fitted together with a standard 29/42 mm glass-tapered joint. The outer glass platinum-tube serves as the anode, while the cathode is a hollow cylinder of sheet platinum. The platinum glass seal consists of joining the platinum tube (2.5 cm OD, 5 cm long, 0.0025 cm wall thickness) to the glass by using a graded glass seal.

This cell was immersed in a methyl alcohol-dry ice bath so that the cross-arm was below the level of the refrigerant. A glass cloth diaphragm (Owens-Corning Fiberglas No. 118) was used to separate the cathode product, hydrogen, from the anode product, a mixture of ozone and oxygen.

Cell With Internally Cooled Platinum-Iridium Anode

A cell (Cell No. 2) having an internally-cooled 95 per cent platinum-5 per cent iridium tubular anode is shown in Fig. 2. The anode (25 cm × 0.3 cm OD × 0.025 cm wall thickness) and the sheet platinum cathode were separated with Teflon spacers. No provision was made for the separation of the hydrogen and ozone-oxygen mixture. Four ports were made in the top, one for the electrolyte thermocouple, one for the cathode connection, and two for the tubular anode. Dow-Corning silicone stop-cock grease was used as the lubricant.

Methyl alcohol, cooled by pumping through a copper coil and storage cylinder immersed in a methyl alcohol-dry ice bath (*ca.* −80°C), was used as the internal refrigerant for the anode (Fig. 3). To further assist in the refrigeration, the entire cell was immersed in a dry ice-40 weight per cent perchloric acid bath.

The absorbers, shown in Fig. 3, were constructed from standard 34/45 mm glass joints. Two were used in series to insure complete absorption of the ozone in the potassium iodide absorbent.

All seals of the absorber and vacuum apparatus were either standard taper glass seals or stopcocks. The other seals used were ¼ in. (0.6 cm) Tygon

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tubing, an ozone-resistant elastomer. Vacuum was maintained by an oil seal vacuum pump. The apparatus was designed so that vacuum could be maintained on the cell while the ozone-absorbing tubes were being drained and refilled.

The cell was filled with 40 weight per cent perchloric acid electrolyte. Dry ice and methyl alcohol were added to the reservoir and the circulating pump turned on. To attain steady-state conditions, the cell was permitted to operate for at least one hour before any samples were taken. Each absorber contained a mixture of 40 ml of 2*M* KI and 10 ml of distilled water. The duration of each run was five minutes, timed by a stop watch. The temperature was controlled by adding dry ice to the bath, the flow rate of the refrigerant being controlled with a valve and by-pass arrangement. Temperatures were determined with standard copper-constantan thermocouples and a Leeds & Northrup No. 8662 precision potentiometer. After absorption of ozone, the absorbent solution was washed into a 500 ml erlenmeyer flask and the liberated free iodine was titrated with standard sodium thiosulfate solution.

Determination of Ozone

Boelter, Lash, and Putnam (2) have recently standardized the potassium iodide method by an absolute method and have reported the conditions necessary for determination of ozone in concentrated mixtures of electrolytic ozone. It has been shown that in this case it is necessary to add strong acid before titration.

Ozone was determined by absorbing in 40 ml of 2*M* potassium iodide solution and 10 ml distilled water, followed by acidification with 10 ml of 6*N* H_2SO_4, and titrating the liberated free iodine with standard sodium thiosulfate solution (2). Current efficiencies were calculated on the basis that both oxygen and ozone have an equivalent weight of 8.

Discussion of Results

With Cell No. 1, hydrogen-free ozone-oxygen mixtures could easily and uniformly be obtained having more than 20 weight per cent of ozone. The yield increased from essentially no ozone at room temperature to more than 20 weight per cent at an electrolyte temperature of about −50°C, the cell having a 40 weight per cent perchloric acid electrolyte and being immersed in a methyl alcohol-dry ice bath. Anode current densities of 10 to 40 amp/dm² gave good results. When 100 ml of the ozone-oxygen anode product were absorbed in alkaline pyrogallol, no trace of undissolved hydrogen remained. When attempts were made to replace the platinum cathode with lead, corrosion of the lead caused difficulties. It is possible, however, that with a continuously

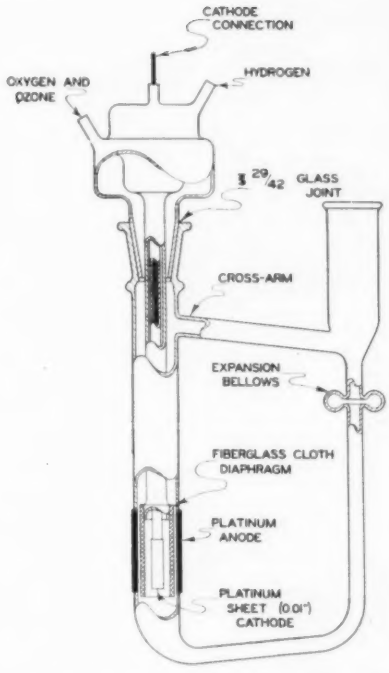

Fig. 1. Cell for preparation of hydrogen-free ozone

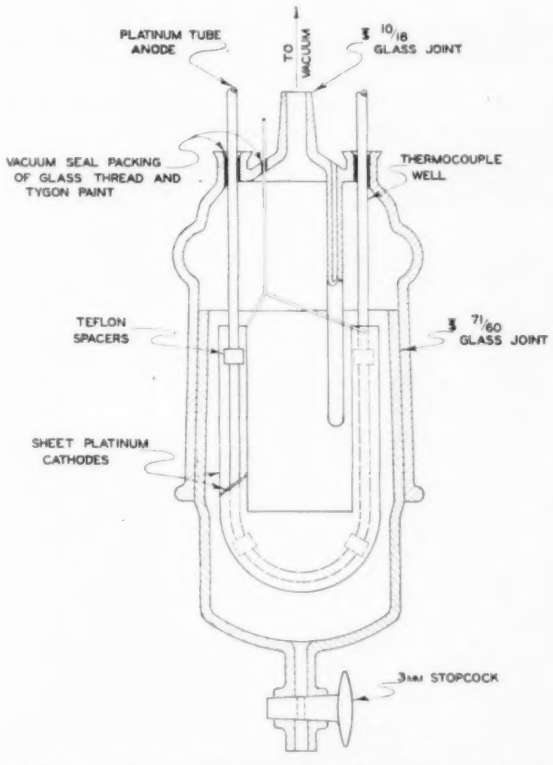

Fig. 2. Cell with internally cooled platinum-iridium anode. The cathode consisted of two sheets of platinum, one on each side of the tubular anode.

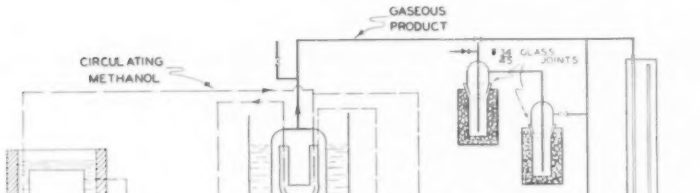

FIG. 3. Flow sheet of system

FIG. 4. Ozone current efficiency as a function of anode temperature at atmospheric pressure.

TABLE I. *Ozone current efficiency as a function of current density and anode temperature at atmospheric pressure. Cell No. 2*

Avg anode temp °C	Anode current density (amp/dm²)	Volts	Ozone current efficiency, %	Weight % ozone	Grams of ozone per kwhr*
−31	29.5	4.60	6.41	5.70	4.12
−31.5	40.9	5.05	8.59	7.64	5.06
−31.5	50.9	7.02	10.16	9.04	6.00
−40.9	29.8	5.20	11.59	10.30	6.64
−40.9	41.2	5.21	14.20	12.63	7.75
−41	49.8	6.10	18.60	16.54	9.24
−50	30.8	5.40	14.75	13.12	8.12
−50	41.3	5.82	18.95	16.85	9.70
−50.7	49.9	6.30	22.90	20.40	10.85
−59.8	31.0	7.70	22.30	19.82	8.77
−59.1	41.1	7.78	27.75	22.90	9.87
−59.8	50.1	7.40	28.20	25.10	11.33

* Does not include power necessary for refrigeration.

operating cell, the platinum cathode could be replaced with lead.

Effect of the Anode Temperature

Cell No. 2 was used primarily to study the effects of anode temperature, current density, and absolute

FIG. 5. Ozone current efficiency vs. current density

pressure above the electrolyte on the ozone concentration and yields.

In all cases the ozone current efficiency and energy yields increased with decreasing anode temperature. Fig. 4 shows the effect of the anode temperature. That the plots are linear is due to the fact that temperature range was small (7). The average anode temperature was determined by two copper-constantan thermocouples in contact with the platinum anode at positions entering and leaving the cell.

The electrolyte was maintained six to ten degrees warmer than the average anode temperature. The lower limit of the temperature is the freezing point of the electrolyte (−56°C).

Effect of the Current Density

In previous work with uncooled anodes and constant bulk electrolyte temperature, current density did not appear to be an important variable (7). When the anodes are not cooled by direct contact with a refrigerant, the anode-electrolyte temperature differential increases with increasing current density

(1), and this would tend to decrease the yield at constant *anode* (not electrolyte) temperature.

Fig. 5 clearly shows the effect of current density on the ozone current efficiency at constant anode temperature, and at atmospheric pressure. At an anode temperature of −50°C, increase in the current density from 30 to 50 amp/dm² increased the ozone current efficiency from 16 to 23 per cent.

The logarithm of the current efficiency is a linear function of the anode temperature, the curves being of approximately the same slope as the curves obtained by plotting current efficiency vs. electrolyte temperature (7).

Energy Yields and Ozone Concentration

Energy yields are a function of two opposing factors. With decrease in the electrolyte and the anode temperatures, the energy yield and ozone current efficiency increase. In addition the resistance of the cell increases with decreasing temperature due to the increased viscosity of the electrolyte.

Conditions for maximum ozone concentration (58 weight per cent) are as follows: 40 weight perchloric acid electrolyte, average anode temperature −62° to −65°C; bulk electrolyte temperature should approach the freezing point (−56°C); anode current density, 0.13 to 2.6 amp/dm²; voltage 8 to 13; and a total absolute pressure above the electrolyte from 10 to 100 mm Hg. Because of entrainment of the electrolyte at lower pressures, it was necessary to limit the average anode current density. It is possible that much of the anode was covered with a film of frozen electrolyte, insulating parts of the anode and locally increasing the current density. Lowering the pressure causes some increase in yield (7).

For maximum energy yields (24 grams ozone per kwhr) the conditions are very similar to those for maximum ozone concentration with the exception of the bulk electrolyte temperature. In this case it should be a few degrees above its freezing point, in order to lower the cell resistance, and the voltage required is 8 volts. Recommended electrolyte temperature is −50° to −53°C for the maximum energy yields.

Conclusions

The following conclusions are drawn from this study:

1. By electrolysis of 40 weight per cent perchloric acid at low temperatures, low pressures, and with refrigerated anodes, ozone energy yields up to 24 g/kwhr, and concentrations up to 58 weight per cent ozone have been obtained.
2. Ozone concentration is a function of the anode temperature. Lowering the anode temperature increases the ozone concentration and the energy yields.
3. At constant anode temperature, increasing the current density increases the ozone concentrations and energy yields.

Acknowledgments

We are indebted to Mr. Ray Newbury for skillful construction of the glass to platinum seal of Cell No. 1. Mr. Newbury also performed all of the other glass-blowing work connected with this project. The Owens-Corning Fiberglas Corporation supplied the glass cloth.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1951 issue of the Journal.

References

1. T. R. Beck and G. L. Putnam, *Ind. Eng. Chem.* (In Press).
2. E. D. Boelter, E. I. Lash, and G. L. Putnam, *Anal. Chem.*, **22**, 1533 (1950).
3. H. Boer, *Rec. trav. chim.*, **67**, 217 (1948).
4. E. Briner and A. Yalta, *Helv. Chim. Acta*, **24**, 1328 (1941).
5. *Ibid.*, **25**, 1188 (1942).
6. F. Fischer and K. Massenez, *Z. anorg. Chem.*, **52**, 229 (1907).
7. G. L. Putnam, R. W. Moulton, W. W. Fillmore, and L. H. Clark, *J.(and Trans.) Electrochem. Soc.*, **93**, 211 (1948).

Amperometric Titrations with *m*-Nitrophenylarsonic Acid[1]

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ABSTRACT

In connection with the amperometric titrations of metal ions with arsonic acids, the polarography of certain arsonic acids has been studied. The arsonic acids are reduced to substituted arsines in a six-electron reduction. The nitro group of *m*-nitrophenylarsonic is reduced in two steps: (*a*) nitro to hydroxylamine involving four electrons and (*b*) hydroxylamine to amine involving two electrons. The effect of hydrochloric acid concentration on these reductions is discussed.

m-Nitrophenylarsonic acid is a suitable reagent for the amperometric titrations of uranyl, thorium, zirconium, and stannic tin. The compositions of the precipitates at the end point are UO_2R, ThR_2, ZrR_2, and SnR, respectively (reagent denoted as H_2R). Zirconium first precipitates as the monoarsonate which is readily transformed into the diarsonate by excess reagent. SnR reacts slowly with an excess of reagent to form $SnR_{1.5}$. Qualitatively, titanium (IV) behaves like tin (IV), but an amperometric titration of titanium is not feasible. Thorium reacts directly to form the diarsonate.

The amperometric titrations described permit direct determination of UO_2, Th, Zr, and Sn (IV).

Introduction

Phenylarsonic acid and other arsonic acid derivatives have been used as analytical precipitants for a number of metals, particularly zirconium (1, 2, 3, 4), thorium (1), titanium (3), tin (5, 6), and bismuth (7, 8). With nearly all these metals the composition of the precipitates is not known and the precipitates are ignited to the metal oxide for weighing. No satisfactory volumetric method has been reported in which these reagents have been used.

A study of the amperometric titration of the metals forming precipitates with arsonic acids is not only of analytical importance, but is also of general chemical interest, as it yields information on the composition of the precipitate, its solubility, its stability under various conditions, coprecipitation phenomena, etc.

Phenylarsonic acid and most of its derivatives are not suitable as reagents in amperometric titrations under various conditions. However, nitrophenylarsonic acid, being polarographically tagged with a nitro group, is very suitable as a reagent in amperometric titrations.

The present paper discusses the polarography of some phenylarsonic acids and the use of *m*-nitrophenylarsonic acid in the amperometric titration of a number of metals. The study is not exhaustive from the analytical point of view in as far as interferences and separations have not been investigated in detail.

Equipment and Reagents

Most of the polarographic measurements were made with a manual instrument. Some polarograms were recorded with a Sargent Model XXI Polarograph. The reference half-cell was the saturated calomel electrode (S.C.E.); electrolytic contact was made by a salt-agar bridge. Measurements were made at 25°C.

The phenylarsonic acid and *m*-nitrophenylarsonic acid used were products of Eastman Kodak Company and were purified by recrystallization from water. The sodium salt of *p*-hydroxyphenylarsonic acid was prepared by Horace Davis of this laboratory according to the procedure in "Organic Syntheses" (9). Stock reagent solutions were prepared by dissolving the reagent in distilled water.

Polarography of Phenylarsonic Acids

The polarography of a number of aromatic arsonic acids has been reported by Breyer (10) He used 0.01*M* arsonic acids in a 0.1*M* lithium chloride medium and in a citrate buffer of *p*H 2.97. The half-wave potentials are reported by him to be between −1.2 v and −1.5 v vs. normal calomel electrode at *p*H 2.97 while those in the unbuffered solutions are 0.01 to 0.02 v more negative. The shape of the polarograms differs considerably among the compounds studied. Although the waves are poorly developed, all reach a limiting current in 0.1*N* lithium chloride. The heights of the waves show more variation than might be attributed to differences in diffusion coefficients, but no interpre-

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tation is offered by Breyer. It is noteworthy that the limiting currents of 0.01M phenylarsonic acids in 0.1N lithium chloride are about one-fifth as great as those found in moderate concentrations of strong acid in this laboratory. Apparently, the diffusion current is not fully developed in the unbuffered salt solutions (*v.i.*). Also, in the unbuffered medium, the decreased acidity at the electrode surface, resulting from the arsonic acid reduction, may affect the half-wave potential.

Our results on the polarographic behavior of phenylarsonic acids at various acidities are summarized in Table I. The half-wave potentials are referred to the S.C.E. The diffusion current data are reported in terms of $i_d/Cm^{2/3}\ t^{1/6}$, which is called the "diffusion current constant" by Lingane (11) and which is independent of the capillary characteristics.

Fig. 1 illustrates the effects of variation in acidity upon the polarographic waves of the arsonic acids. It shows that the arsonic acid wave is fully developed only within relatively narrow limits of acidity. The diffusion current corresponds to a six-electron reduction:

$$-AsO_3H_2 + 6H^+ + 6e \rightarrow -AsH_2 + 3H_2O.$$

From the diffusion currents of the acids and the assumption that the wave corresponds to a six-electron reduction, the following diffusion coefficients (in cm²/sec at 25°C) are calculated from the Ilkovic equation: phenylarsonic, 7.6×10^{-6}; *p*-hydroxyphenylarsonic, 6.0×10^{-6}; *m*-nitrophenylarsonic, 7.3×10^{-6}.

These values seem reasonable in comparison with the diffusion coefficient of benzoquinone (12) which is 8.6×10^{-6} cm²/sec. The assignment of six electrons to the arsonic acid reduction is further confirmed by comparison of the diffusion current of the arsonic acid wave with that of the six-electron doublet wave in *m*-nitrophenylarsonic acid as discussed below.

All of the arsonic acid waves studied in this investigation are poorly developed and irreversible waves. The half-wave potentials, in the *p*H range of optimum wave development, shift −0.07 v per unit increase in *p*H. The decrease in limiting currents at lower acidities (*p*H > 2) might be explained on the assumption that only the free undissociated acid, not the arsonate ion, is reduced. The limiting currents in buffers of *p*H 2–4 are somewhat greater than corresponds to the equilibrium concentration of the undissociated acid. The increment may be a kinetic current (13, 14) due to reformation of arsonic acid, as the latter is removed by reduction at the surface of the electrode.

The arsonic acid wave can be used for quantitative determination of arsonic acids in 0.1 to 1N hydrochloric acid as supporting electrolyte if the apparent diffusion current is corrected for residual current and if it is measured at the proper potential (see Fig. 1). However, because of the above limitations, arsonic acids, with the exception of the nitro derivatives, are not suitable for amperometric titrations.

Polarograms of *m*-nitrophenylarsonic acid in media of various hydrogen ion concentrations are shown in Fig. 2. In moderate concentrations of strong acid, e.g., 0.2N hydrochloric acid, the nitro group yields two waves; at lower concentrations of hydrogen ion, e.g., *p*H 3, one wave only appears, the height of which is equal to that of the first wave in more concentrated acid medium. In 0.1 to 1N hydrochloric acid the diffusion current of the second part

TABLE I. *Polarographic characteristics of aromatic arsonic acids*

Acidity	$E_{\frac{1}{2}}$ (S.C.E.)	$i_d/(Cm^{\frac{2}{3}}t^{\frac{1}{6}})$
Phenylarsonic acid. Concentration: $9.31 \times 10^{-4}M$		
6N HCl	(−0.59*)	(3.2*)
1N HCl	−0.89	9.9
0.2N HCl	−0.94	9.9
0.1N HCl	−0.96	10.0
0.05N HCl	−0.98	10.1
Citrate buffer *p*H 3.0	−1.18	9.4
Citrate buffer *p*H 3.9	Hydrogen-wave interferes badly	
p-Hydroxyphenylarsonic acid. Concentration: $7.08 \times 10^{-4}M$		
6N HCl	(−0.60*)	(7.3*)
1N HCl	−0.84	7.8
0.2N HCl	−0.91	8.7
0.05N HCl	−0.94	8.8
*p*H 3.0 (citrate)	(1.20*)	(7.8*)
*p*H 3.9 (citrate)	Hydrogen-wave interferes badly	
m-Nitrophenylarsonic acid $3.83 \times 10^{-4}M$		
0.1N HCl	−0.92 (refers to arsonic wave)	19.6**

* These values are less accurate than the others because of interference of the hydrogen-wave with development of the limiting current.

** Twelve electron reduction of both the nitro group and the arsonic acid group.

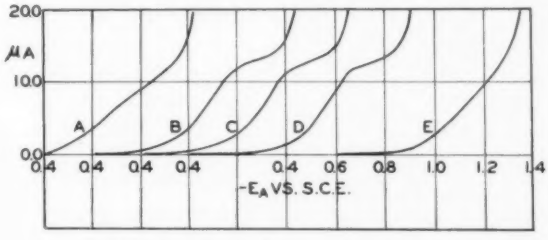

FIG. 1. Effect of hydrochloric acid on the arsonic acid wave of $7.08 \times 10^{-4}M$ *p*-hydroxyphenylarsonic acid. HCl concentrations: (A) 6N, (B) 1N, (C) 0.2N, (D) 0.05N, (E) *p*H 3.0 (citrate buffer).

of the nitro doublet wave is one-half that of the first. The total diffusion current of the doublet nitro wave is equal to that of the arsonic acid wave. Evidently the following reactions account for the various waves:

First wave: $-NO_2 + 4H^+ + 4e \rightarrow -NHOH + H_2O$

Second wave: $-NHOH + 2H^+ + 2e \rightarrow -NH_2 + H_2O$

Third wave: $-AsO_3H_2 + 6H^+ + 6e \rightarrow -AsH_2 + 3H_2O$

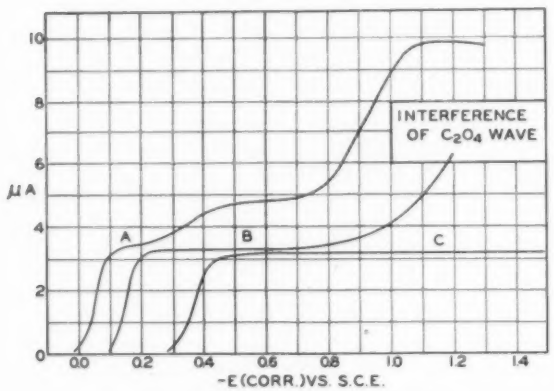

FIG. 2. Effect of *p*H on the nitro waves of $2.27 \times 10^{-4}M$ *m*-nitrophenylarsonic acid. (A) *p*H 0.9 in HCl; (B) *p*H 2.9 in oxalate buffer; (C) *p*H 6.9 in ammonium acetate.

The half-wave potentials of the nitro to hydroxylamine waves in media of various hydrogen ion concentrations are as follows:

Medium	$E_{\frac{1}{2}}$ vs. S.C.E.
0.2*N* Hydrochloric acid	−0.055 v
Oxalate buffer: *p*H 2.9	−0.147
Ammonium acetate: *p*H 6.9	−0.370
1*N* Sodium hydroxide	−0.70

It is seen that $E_{1/2}$ of the first nitro wave decreases approximately 0.05 v per unit increase in *p*H. The half-wave potential of the second nitro wave (hydroxylamine to amine) in 0.2*N* hydrochloric acid is −0.33 v vs. S.C.E.

Both of the nitro diffusion currents have been successfully used for quantitative polarographic determinations and for amperometric titration measurements. When the hydrogen ion concentration is greater than 1*N*, the first nitro wave is not well developed, and measurement of the diffusion current of the six-electron doublet wave is recommended. However, at smaller acid concentrations, the four-electron (first) diffusion current is superior to the six-electron (doublet) diffusion current for quantitative purposes. Note that there are significant variations of the wave characteristics with acidity. Hence, in quantitative methods employing different acidities, diffusion current measurements must be made at correspondingly different potentials.

Amperometric Titration with *m*-Nitrophenylarsonic Acid

Apparatus.—A manual polarograph was used for all amperometric measurements. The titration cell was equipped with a gas inlet tube which caused the nitrogen to impinge on the bottom of the cell, thus agitating the precipitate as it settles and providing thorough mixing. The cell was covered with a three-hole stopper which accommodated the salt bridge, dropping mercury electrode, and buret tip. A Kimble Normax 10-ml buret with $\frac{1}{20}$-ml graduations was used for addition of reagent. A saturated calomel electrode was used as a reference electrode.

General procedure.—Make up the mixture to be analyzed in a 100-ml volumetric flask and dilute to volume. Transfer a 25-ml aliquot to an amperometric titration cell. Pass oxygen-free nitrogen through the solution for 10–15 minutes. Add 0.5 to 1.0 ml standard *m*-nitrophenylarsonic acid. When the nitrogen has passed through the solution for ten minutes, measure the current at the appropriate potential. Make further additions of reagent and corresponding current measurements so that three to five measurements are made on each side of the end point. Pass nitrogen through the solution after each addition for sufficient time to allow the reaction to reach or approach equilibrium. At the end of the titration, correct the measured currents for dilution by the added reagent and plot the titration lines to determine the end point.

The *m*-nitrophenylarsonic acid reagent may be standardized against a known amount of metal ion by the amperometric method or against standard base by the potentiometric method.

Titration of Uranyl Ion

Uranyl ion reacts with *m*-nitrophenylarsonic acid in slightly acid medium to form insoluble, yellow uranyl nitrophenylarsonate, $UO_2C_6H_4NO_2AsO_3$. No analytical application of this reaction has been reported in the literature.

The standard uranyl solution used in these experiments was prepared from Merck Reagent Grade uranyl nitrate hexahydrate. The stock solution was standardized by precipitation of ammonium biuranate and ignition to U_3O_8.

In these titrations, best results are obtained when the titrations are carried out in acetate buffers. In the buffers employed, uranyl yields one polarographic wave. When gelatin is added as a maximum suppres-

sor, the wave is well developed and the diffusion current is well defined.

The half-wave potential of the uranyl in the acetate buffer is −0.31 v vs. S.C.E. A diffusion current is found between −0.50 and −0.80 v. In the amperometric titration of uranyl with nitrophenylarsonic acid, the current measurements are made at −0.50 to −0.55 v. At these potentials, uranyl yields a diffusion current before the end point and the nitro reagent a four-electron diffusion current beyond the end point.

Because of the complexing action of the acetate ion on uranyl and consequent effect on the solubility of the uranyl salt, the concentration of the acetate ion should not exceed 0.050*M*. On the other hand, if the concentration of acetate ion is less than 0.025*M*, the titration curve preceding the end point is not well defined. The *p*H should be controlled between 4.0 and 4.5. At higher *p*H, the results are low due to formation of basic uranyl salts. At lower *p*H values the solubility of uranyl arsonate is too great to yield a satisfactory titration.

The results of some titrations of 0.005*M* uranyl solutions are shown in Table II. The calculated amount of reagent is 3.13 ml. The amount found (in the absence of neutral salts) varies from 3.08 to 3.11 ml. Hence, the accuracy is about −1 per cent and the precision about 1 per cent.

Neutral salts, in general, bring about a positive error of about 3 per cent. The error is practically constant for 0.2 to 1.0*M* salt concentrations in titrations of 0.005*M* uranyl as shown in Table II. To eliminate possible salt error due to variation in salt concentration between 0.0 and 0.2*M*, it is recommended in the procedure to make the solutions 0.3*M* in sodium chloride. Also it is noteworthy that, in uranyl titrations, the currents fluctuate considerably when sulfate is present in a concentration of 1.0*M*.

Procedure.—To a sample containing 50–200 mg uranium, as uranyl, add 10 ml acetate buffer, being 0.5*M* in acetic acid and 0.25*M* in sodium acetate, and about 50 ml water. Add 2.0 g sodium chloride and 5 ml 0.1 per cent gelatin. Dilute to 100 ml. Titrate with *m*-nitrophenylarsonic acid solution which has been standardized against known amounts of uranyl in solutions prepared according to the above procedure. Make current measurements at −0.55 v one or two minutes after each addition of reagent.

Results of titrations carried out according to the above procedure are precise to ±1 per cent. They also show a significant trend toward more negative errors with increasing uranyl concentrations. Data are shown in Table III. Typical titration curves are shown in Fig. 3.

TABLE II. *Titration of 25.00 of 0.00503M uranyl with 0.0401M m-nitrophenylarsonic acid in 0.05M acetic acid —0.025M sodium acetate. Effect of indifferent electrolyte.*

Conc of salt	Ml of reagent used		
No salt added	3.08, 3.08, 3.10, 3.11, 3.11		
	NaCl	KCl	NH_4NO_3
0.2*M*	3.23	3.21	3.27
	3.14	3.29	3.21
0.4*M*	3.17	3.23	3.28
	3.19	3.22	3.15
0.6*M*	3.29	3.23	3.30
	3.17	3.23	3.26
1.0*M*	3.30	3.31	3.17
	3.25	3.29	3.29

TABLE III. *Titration of uranyl*

Conc of reagent: 0.0339*M*
Titration medium: 0.3*M* NaCl; 0.005% gelatin
0.025*M* NaAc–0.050*M* HAc

Conc uranyl (molarity)	Relative % error* observed
0.00400	+2.0
0.00500	+1.9
0.00600	+1.2
0.00700	0.0
0.00900	0.0
0.01000	−0.2
0.01200	−1.1
Mean error	+0.55
Mean deviation from mean	±1.0%

* Reagent titer determined amperometrically with 0.00700*M* uranyl.

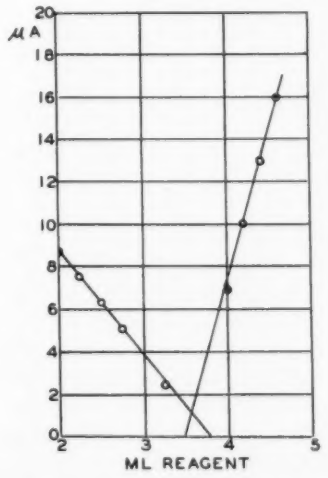

FIG. 3. Typical amperometric titration curve of 0.00509*M* uranyl nitrate with 0.0350*M* *m*-nitrophenylarsonic acid in 0.025*M* sodium acetate—0.050*M* acetic acid. $E_a = -0.7$ v.

Titration of Thorium

Precipitation of thorium with phenylarsonic acid has been described by Rice, Fogg, and James (1). The results of the present investigation show that it is possible to titrate thorium with *m*-nitrophenylarsonic acid amperometrically. Thorium diarsonate is formed during the titration. Equilibrium is rapidly attained in this system, and the four-electron nitro diffusion current can be measured within one to two minutes after each addition of reagent. A typical titration curve is shown in Fig. 4.

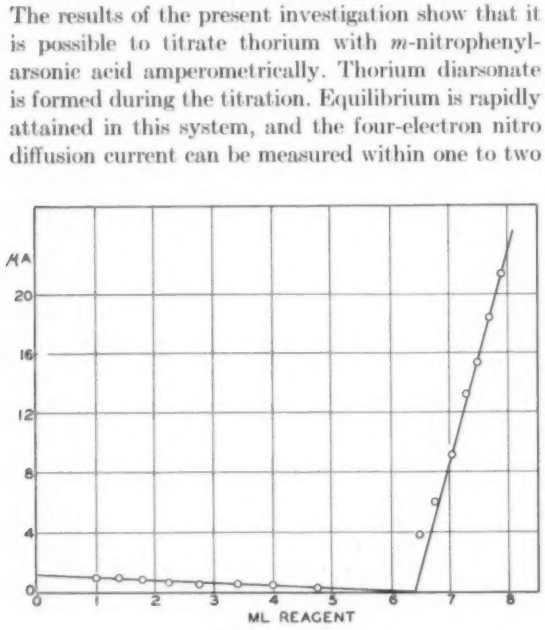

FIG. 4. Typical amperometric titration curve of 0.00502*M* thorium nitrate with 0.0397*M* *m*-nitrophenylarsonic acid in 0.01*M* hydrochloric acid. $E_a = -0.3$ v.

TABLE IV. *Titration of thorium in 0.003M to 0.01M HCl with 0.0398M m-nitrophenylarsonic acid*

Conc of thorium	% Error	% Deviation from mean error
0.00301*M*	+1.8	+0.9
0.00502	+1.4*	+0.5
	+1.1	+0.2
0.00702	+0.6	−0.3
	0.0*	−0.9
0.00802	+0.7	−0.2
0.01003	+0.7	−0.2
Mean error	+0.9	
Mean deviation from mean error		±0.5

* Carried out in 20% alcohol.

The thorium solutions used in these experiments were prepared from pure thorium nitrate tetrahydrate obtained from A. D. Mackay, New York. Samples of this salt were assayed by ammonia precipitation and ignition to the oxide. The results indicate 100.7 per cent purity on the basis of the nitrate tetrahydrate.

The solubility of thorium arsonate is increased by increase of acidity. On the other hand, the hydrolysis of thorium increases with decrease of acidity. In 0.1*N* hydrochloric acid, no satisfactory titration lines were obtained. In 0.005*N* to 0.01*N* hydrochloric acid, good results were obtained if the solutions were titrated when freshly prepared. Thorium solutions in moderately concentrated acid can be neutralized to *p*H 2.5 with dilute ammonia and were found to give good results when titrated immediately after neutralization. It is advisable to neutralize the arsonic acid reagent to *p*H 2.5 for use in this titration.

Alkali and ammonium salts of chloride, sulfate, and nitrate in concentrations less than 1*M* do not affect the results of the titration.

The addition of alcohol does not improve the result.

Procedure.—Dissolve a sample containing 0.1–0.3 g thorium in a little water acidified with 1 ml 1*N* hydrochloric acid; then add 10 ml 0.5*M* ammonium chloride. If the thorium is in solution with a considerable amount of acid, carefully neutralize the solution to *p*H 2.0–2.5 with dilute ammonium hydroxide. In either case, make the final solution to 100 ml. Titrate the freshly prepared thorium solution with *m*-nitrophenylarsonic acid reagent which has been neutralized to *p*H 2.5. Make current measurements at −0.30 v, and allow one to two minutes after each addition of reagent for attainment of equilibrium.

The results of titrations of various concentrations of thorium according to the recommended procedure are given in Table IV. It is seen that in a concentration range of thorium between 0.003 and 0.01*M* the mean error is +0.9 per cent and the mean deviation from the mean error is ±0.5 per cent.

Titration of Zirconium

Zirconium has been determined by precipitation with various arsonic acids and ignition to the oxide (1, 2, 3, 4). Under specified conditions it has been found possible to obtain well-defined titration curves for the titration of zirconium with *m*-nitrophenylarsonic acid. The product at the end point contains somewhat more than two moles of arsonate per mole of zirconium, and its composition is quite dependent on the acidity.

The source of zirconium for these experiments was pure zirconium nitrate obtained from A. D. Mackay, New York. This was converted to the zirconyl chloride octahydrate. Stock zirconyl solutions were prepared from the latter and standardized by the cupferron method.

In the titration, equilibrium is attained slowly upon first additions of reagent, but with the accumulation of precipitate in the system, the rate of attainment of equilibrium is increased. Addition of a suspension of washed zirconium diarsonate hastens

attainment of equilibrium somewhat in the early stages of the titration.

In this investigation, the amperometric titrations of zirconium were carried out in hydrochloric acid medium. It was found that the acid concentration should be great enough to prevent formation of basic zirconium salts, which leads to low and irreproducible results. In the range of acidities in which the titration was found feasible, the results show a large positive titration error which increases in proportion to the concentration of hydrochloric acid. The addition of alcohol decreases this positive error and improves the titration in general. The data in Table V illustrate these observations.

It is evident that the hydrochloric acid concentration must be closely controlled if reproducible results are to be obtained.

Procedure.—Dissolve a sample containing 0.03 to 0.10 g zirconium in 15.0 ml conc hydrochloric acid and 40 ml water. Add 20 ml ethyl alcohol and 10 ml 0.1 per cent gelatin. Dilute to 100 ml and titrate with standard reagent making current measurements at −0.5 v vs. S.C.E. and allowing one to two minutes after each addition of reagent for attainment of equilibrium. Determine by this procedure the titer of the reagent against known amounts of zirconium.

Results of titrations of various concentrations of zirconium are given in Table VI.

From these data it is apparent that fairly satisfactory results can be obtained in the titration of zirconium under closely controlled conditions.

Titration of Stannic Tin

The gravimetric determination of tin with phenylarsonic acid has been described by Knapper, Craig, and Chandlee (5).

The stannic tin solution used in the titration experiments was prepared from Mallinckrodt R.G. granulated tin metal by treatment with warm, moderately concentrated hydrochloric acid and chlorine gas. The final mixture was 0.1*M* in tin and 1*N* in hydrochloric acid.

The amperometric titration of stannic tin with *m*-nitrophenylarsonic acid is feasible in 0.2–0.3*N* hydrochloric acid at −0.15 v vs. S.C.E. Equilibrium is reached slowly in the system; usually ten minutes should be allowed after each addition of reagent before a reading is taken.

Moderate concentrations of both hydrogen ion and chloride ion are necessary to prevent formation of basic salts. The minimum concentration for each of these ions appears to be 0.2*M*. Increase in concentration of either of these ions increases the solubility of the stannic monoarsonate and results in a poorer titration curve. Best results are obtained in samples containing 0.06 to 0.12 g of tin in 100 ml solution.

Procedure.—Take for analysis a sample containing 0.06 to 0.12 g tin in the stannic state. Add sufficient acid and water to make the solution 0.2 to 0.3*N* in hydrochloric acid and the final volume 100 ml. Titrate amperometrically at −0.15 v allowing 10–15 minutes for equilibrium to be reached after each addition of reagent up to the end point.

From one and one-half to two hours is required for a titration. However, two or three titrations may be carried out simultaneously without a much greater time requirement. Results of some titrations are shown in Table VII.

The rather unsatisfactory precision in this method

TABLE V. *Effects of hydrochloric acid and alcohol on the titration of 0.00548M zirconium with 0.0400M m-nitrophenylarsonic acid*

Conc HCl	Per cent titration error	
	Without alcohol	20% Alcohol
0.6*N*	Indeterminate end point	+0.2%
1.2*N*	+7.5	+2.0
1.8*N*	+11.5	+5.8
2.4*N*	+12.8	+8.7

TABLE VI. *Titrations at various zirconium concentrations with 0.0400M m-nitrophenylarsonic acid in 20% alcohol, 1.8N HCl, and 0.01% gelatin*

Conc Zr	Relative error in %	
	Column A*	Column B‡
0.0044*M*	+7.5	+2.2
0.0055*M*	+5.6	+0.3
0.0066*M*	+4.9	−0.4
0.0077*M*	+3.4	−1.9
0.0088*M*	+5.6	+0.3
0.0099*M*	+4.7	−0.6
0.0110*M*	+5.2	−0.1
Mean error (A) or deviation (B)	+5.3%	±0.8%

* Results based on reagent titer obtained from titration with standard base.

‡ Results based on mean reagent titer obtained from amperometric titration of known amounts of zirconium by the procedure outlined above.

TABLE VII. *Titration of stannic tin with 0.04M reagent in 0.25N HCl*

Tin conc	% Relative error (deviation from mean)
0.00510*M*	−1.6
0.00612*M*	+1.8, −2.0
0.00714*M*	−0.5, −1.4
0.00817*M*	−0.9, −1.1
0.00918*M*	+1.1, +2.4, +3.3
0.01020*M*	−0.7, −0.7
Mean deviation from mean	±1.5%

may be attributed largely to the uncertainty of the values on the precipitation line. These values are not true equilibrium values but for practical purposes are taken at a time when the rate of change of current with time has become nearly constant.

Titrations of Titanium and Bismuth

Determinations of titanium (3) and bismuth (7, 8) gravimetrically with phenylarsonic acids have been recommended In the present study, amperometric titrations of these metals with *m*-nitrophenylarsonic acid have not been found to be feasible. In acid concentrations great enough to prevent formation of basic bismuth compounds of indefinite composition, bismuth arsonate is so soluble that good amperometric titration lines are not obtained. In amperometric titrations of titanium, the product at the end point has been found to vary in composition between 1 and 1½ moles of arsonate per mole titanium. Under all conditions tried, the results were irreproducible.

Compositions of Nitrophenylarsonates Formed during Titrations

It is evident from amperometric titrations that when *m*-nitrophenylarsonic acid is gradually added to stannic tin a monoarsonate is formed. Titanium reacts in the same fashion as has been shown by adding various amounts of reagent to titanic solutions and determining the unreacted titanium in the supernatant liquid. Similar experiments have been carried out with zirconium in 1*N* hydrochloric acid and with thorium in 0.01*N* hydrochloric acid. In these experiments the unreacted metal ions were determined by ammonia precipitation. The results indicate that the zirconium is first precipitated as the monoarsonate with *m*-nitrophenylarsonic acid and that the thorium is precipitated as the diarsonate without first forming the monoarsonate.

It is thought that the monoarsonates may be formed by simple displacement reactions involving chloro complexes or oxy-ions of the metal, viz.,

$$SnCl_2^{++} + H_2R \rightarrow SnCl_2R + 2H^+$$
$$TiO^{++} + H_2R \rightarrow TiOR + 2H^+$$

in which H_2R is the reagent.

The tin precipitate was analyzed for chloride. Dependent upon the mode of washing of the precipitate, the chloride content varied between 0.6 and 0.3 mole per mole tin. Apparently the precipitate, is a mixture of $SnOR$ and $SnCl_2R$ or of $Sn(OH)_{(2-z)}Cl_zR$.

Reaction of the Monoarsonate with Excess Reagent

Formation of the diarsonates of thorium and zirconium is observed under the conditions described. From evidence given above, it is known that zirconium is precipitated first as the monoarsonate, and it is apparent that the formation of the diarsonate involves addition of a second mole of reagent to the monoarsonate Since the latter reaction takes place rapidly, it is not distinguishable from the primary reaction in an amperometric titration. With stannic tin, however, the secondary reaction takes place relatively slowly. Consequently, the stannic tin may be titrated amperometrically to the monoarsonate end point without interference from the secondary reaction. Upon shaking with a 25 per cent excess of reagent, the monoarsonate combines very slowly with the excess arsonic acid, and at equilibrium the reagent concentration is nearly that found when tin is in excess during formation of the monoarsonate. Addition of reagent beyond this concentration brings about a definite increase in the equilibrium concentration of reagent.

Since the reagent concentration does not remain constant during the formation of the second compound, it is doubtful that a separate second solid phase is produced. The formula of the second compound appears to be $SnR_{1.5}$. If this product is in solid solution equilibrium with the monoarsonate and reagent, the following relationship should exist:

$$K = \frac{(SnR_{1.5})}{(SnR)(R)^{0.5}}.$$

TABLE VIII. *The reaction of SnR with m-nitrophenylarsonic acid*

Medium: 0.25*N* HCl

Reagent added / Sn added	Molar reagent Conc	$\frac{(SnR_{1.5})}{(SnR)}$	$\frac{(SnR_{1.5})}{(SnR)\ (R)^{0.5}} = K$
(molar ratio)	*(after 12 days)*		
1.25	0.067	0.17	0.66
1.50	0.27	0.34	0.65
1.75	0.68	0.42	0.51
2.00	0.93	0.64	0.67
2.25	1.62	0.55	0.43
2.50	1.94	0.77	0.55

To test this hypothesis a few values of K have been calculated from the experimental data. The results are shown in Table VIII and lend support to the solid solution hypothesis.

Titanium monoarsonate reacts similarly to stannic monoarsonate with an excess of *m*-nitrophenylarsonic acid. The secondary reaction is much more rapid in the case of titanium and is not distinguishable from the primary reaction in an amperometric titration.

Summary

Concentrations of hydrochloric acid are given at which the arsonic group in arsonic acids is reduced at the dropping electrode to the arsine group. This

reaction involves six electrons. *m*-Nitrophenylarsonic acid is a suitable reagent for the amperometric titration of some cations which precipitate as arsonates. In such titrations the excess of reagent line is determined at potentials at which the nitro group is reduced to the hydroxylamine (4 electrons) or to the amine (6 electrons). Procedures are given for the amperometric titration of uranyl, thorium, zirconium, and stannic tin. With the reagent denoted as H_2R, the composition of the precipitates at the end point correspond to UO_2R, ThR_2, ZrR_2, and SnR, respectively. Zirconium first precipitates as the monoarsonate which is readily transformed into the diarsonate by an excess of reagent. SnR reacts slowly with an excess of reagent to give $SnR_{1.5}$. Qualitatively, titanium (IV) behaves like tin (IV). Thorium reacts directly to form the diarsonate.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the JOURNAL.

REFERENCES

1. A. C. RICE, H. FOGG, AND C. JAMES. *J. Am. Chem. Soc.*, **48**, 895 (1926).
2. F. W. ARNOLD AND G. C. CHANDLEE. *J. Am. Chem. Soc.*, **57**, 8 (1935).
3. C. T. SIMPSON AND G. C. CHANDLEE, *Ind. Eng. Chem. Anal. Ed.*, **10**, 642 (1938).
4. R. CHANDELLE, *Bull. soc. chim. Belges*, **46**, 283 (1937).
5. J. S. KNAPPER, K. A. CRAIG, AND G. C. CHANDLEE, *J. Am. Chem. Soc.*, **55**, 3945 (1933).
6. V. I. KUTSNESOV, *J. Applied Chem.* (*U.S.S.R.*), **13**, 1512 (1940).
7. A. K. MAJUMDAR, *J. Indian Chem. Soc.*, **21**, 120 (1944).
8. A. K. MAJUMDAR, *J. Indian Chem. Soc.*, **22**, 313 (1945).
9. O. KAMM, "Organic Syntheses," Vol. IV, J. Wiley & Sons, Inc., New York (1925).
10. B. BREYER, *Ber.*, **71**, 163 (1938).
11. J. J. LINGANE, *Ind. Eng. Chem. Anal. Ed.*, **15**, 588 (1943).
12. I. M. KOLTHOFF AND J. J. LINGANE, "Polarography," p. 190, Interscience Publishers, Inc., New York (1941).
13. R. BRDICKA AND K. WIESNER, *Coll. Czechoslov. Chem. Communs.*, **12**, 138 (1947).
14. I. M. KOLTHOFF AND A. LIBERTI, *J. Am. Chem. Soc.*, **70**, 1885 (1948).

The Electrodeposition of Copper-Lead Alloys[1]

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ABSTRACT

A number of solutions from which copper-lead alloys might be deposited were investigated. The most promising of these, a cyanide-tartrate solution, was studied in detail. The effects on alloy composition, single metal potentials, and alloy potentials were determined for all of the possible variables, using a rotating cathode setup. The alloys were hard and brittle except those containing a high percentage of lead. Reproducibility was satisfactory at any given time, but the lead content of the deposits increased as the solution aged.

Introduction

Copper-lead alloys are manufactured at the present time either by casting or by the method of powder metallurgy. One very important use for this type of alloy, containing from 60–70 per cent copper, is for automotive bearing liners. An electrodeposition process would offer definite advantages over these other methods.

Certain difficulties in the commercial electrodeposition of copper-lead alloy possessing the requisite properties are readily forseen. The solid solubilities are unfavorable, the alloy being primarily of the mixture type. The normal electrode potentials are relatively far apart, thus making electrodeposition from simple salt solutions impossible except where high polarization of the more noble metal is involved. Many of the salts of these metals, especially those of lead, are insoluble, thus limiting the anions which may be present in the solution. Relatively thick deposits are required for practical purposes, in which case the solution would have to be suitable for high speed plating. This means that a large reserve of the two metal ions in the solution must be maintained. The chemical and physical variables must not be too critical.

There have been a number of reports of copper-lead alloy deposition during the past fifteen years. Marino (1) patented a process for plating copper-lead alloys from the metal tartrates, paratartrates, or oxalates in ammonia. Belyaev, Valeeva, and Hel'man (2) and Belyaev, Markova, and Hel'man (3) reported electrodeposition of the alloy from solutions of the benzenedisulfonates. Bagley, Bagley, and Berdan (4) obtained a patent covering the electrodeposition of copper-lead alloys from the fluoborates or fluosilicates of the metals. In the course of their study of the structures of electrodeposited copper alloys, Meyer and Phillips (5) obtained copper-lead alloys by adding sodium plumbite to their standard copper bath. Roszkowski, Hanley, Schrenk, and Clayton (6) reported the electrodeposition of copper-lead alloys from an ethylenediamine solution. Hashimoto (7) described a process for plating bearing surfaces with copper-lead alloy using a solution containing copper nitrate and lead fluosilicate. Bollenrath (8) and Beerwald and Döhler (9) have published results of studies of copper-lead plating baths of the alkaline citrate or tartrate type. Young and Struyk (10) described unsuccessful attempts to plate copper-lead alloys of acceptable quality from fluoborate solutions.

The purposes of the present investigation were: (*a*) the examination of some of the more promising copper-lead alloy plating solutions described in the literature, (*b*) the preparation of new types of solutions, (*c*) the selection of one of these for intensive study, and (*d*) the study of the effects of all of the variables for the solution selected in order to obtain fundamental information which might at some future time be utilized in the development of a commercial copper-lead alloy plating process.

Results of Preliminary Work

Approximately 170 ml of each solution to be tested were placed in a rectangular plastic cell with flat electrodes at each end and subjected to electrolysis under various conditions of temperature, current density, and agitation. The static potentials of copper, lead, and the deposit, and the dynamic cathode potential were measured using a saturated calomel electrode and a precision potentiometer. The deposits were checked for hardness, ductility, brightness, surface structure, and composition.

Many different types of solutions were prepared and electrolyzed. The extent to which each solution

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was investigated was determined by the degree to which it appeared to meet the requirements of a successful copper-lead alloy plating bath. The following solutions showed little promise and were studied only superficially: (*a*) ammonium tartrate, sodium hydroxide, copper acetate, and lead acetate; (*b*) sodium thiosulfate, copper acetate, and lead acetate; (*c*) sodium pyrophosphate, copper acetate, and lead acetate; (*d*) sodium hydroxide, ammonium hydroxide, copper acetate, and lead acetate; and (*e*) sulfamic acid, copper sulfamate, and lead sulfamate.

The solutions which were studied with reasonable thoroughness are listed below with a brief summary of the experimental results obtained with each solution. The compositions given merely indicate the general type of solution since in most cases the solutions were modified as the work progressed in an effort to improve the alloy deposit and to obtain various alloy compositions.

Fluoborate.—The solution described in the Bagley patent (4) contains 240 g/l of hydrofluoric acid, 116 g/l of boric acid, 70 g/l of copper carbonate, and 50 g/l of basic lead carbonate. The static metal potentials were about 0.5 volt apart and no alloy was obtained under normal plating conditions. Alloy deposits were obtained in a still bath containing a high concentration of lead and a very low concentration of copper but these deposits were of poor quality.

Perchlorate.—The solution contained 300 g/l of 72 per cent perchloric acid, 100 g/l of copper carbonate, and 200 g/l of basic lead carbonate. The static metal potentials were about 0.1 volt closer together than in the fluoborate solution but, in general, these two solutions were very similar in their characteristics.

Acetate.—The solution contained 400 g/l of ammonium acetate, 20 g/l of sodium hydroxide, 100 g/l of copper acetate, and 190 g/l of lead acetate. The static metal potentials were about 0.5 volt apart. Due to the high polarization of copper, it was possible to obtain alloy deposits from this solution. The deposit composition was difficult to control and the alloy obtained was only fair in quality.

Cyanide.—The solution contained 560 g/l of sodium hydroxide, 98 g/l of sodium cyanide, 72 g/l of cuprous cyanide, and 227 g/l of lead acetate. The static metal potentials were practically equal but the polarization of copper was so great that only high lead content deposits were obtained.

Tartrate.—The solution contained 200 g/l of sodium potassium tartrate, 400 g/l of sodium hydroxide, 120 g/l of copper acetate, and 232 g/l of lead acetate. The static metal potentials were about 0.4 volt apart, copper being the more noble. The high polarization of copper made it possible to obtain alloy deposits but these deposits were of very poor quality.

Tartrate-citrate.—The solution as given by Bollenrath (8) contained 56 g/l of potassium tartrate, 180 g/l of potassium citrate, 30 g/l of potassium hydroxide, 14 g/l of copper hydroxide, and 58 g/l of lead acetate. The static metal potentials were about 0.2 volt apart, copper being the more noble. Moderately bright and very smooth deposits were obtained but the deposits showed a tendency to develop numerous cracks if the thickness exceeded about 0.025 mm.

Cyanide-tartrate.—The composition of the solution formulated on the basis of rather extensive preliminary work is given in Table I. This was the most promising of the solutions studied and was selected for detailed investigation.

Experimental Methods for Work on Cyanide-Tartrate Solutions

Solutions.—The C.P. chemicals used were weighed to the nearest 0.1 g.

The plating cell.—The container for the plating solution was a 250 ml beaker. A Bakelite baffle fixture consisting of two discs with four symetrically arranged vertical baffle plates between them was placed in the beaker. The inside, beveled edges of the baffle plates were spaced just far enough apart to allow the cylindrical cathode with its deposit to rotate without rubbing. The cathode was inserted through a hole in the center of the top disc and a narrow section of this disc was cut out to provide for the tip of a calomel electrode. The capacity of the cell with the baffle and cathode in place was about 180 ml.

Electrodes.—Hollow cylindrical anodes were used. These anodes were fitted snugly against the inside of the plating cell and served to hold the baffle fixture in place. The anode material was electrolytic copper except in the study of the anode process where copper-lead alloy was used.

Both platinum and polished brass cathode surfaces were used. The brass surface was obtained by slipping a brass cylinder $\frac{1}{32}$ in. (0.08 cm) thick, $1\frac{3}{4}$ in. (4.45 cm) long, and having an OD of $\frac{5}{8}$ in. (1.59 cm) over a threaded steel rod of the proper dimensions. The platinum surface was obtained by placing a platinum cup over a threaded steel rod similar to the one used for the brass cylinders. The threaded steel rod, with either a brass cylinder or a platinum cup in place, was screwed into the lower end of the vertical spindle used to rotate the cathode. Contact was made to the rotating spindle by means of a platinum wire extending into a pool of mercury placed in a small hole drilled into the top of the spindle.

Agitation.—The solutions were stirred by rotating the cathode at a constant, measured speed.

Potential measurements.—A special saturated calomel electrode having a narrow sealed tip was used. A very small hole was blown in the outside of the tip near the sealed end and this hole was placed opposite the center of the cathode (vertically) and at a fixed distance from its surface in all runs. The potential of the cathode during the plating run, the static potential of the alloy, and the potentials of pure copper and pure lead immersed in the solution were measured with reference to the saturated calomel electrode by means of a Queen-Gray precision potentiometer and a Leeds & Northrup lamp and scale galvanometer.

Examination of deposits.—The deposits were checked for relative brightness, smoothness, hardness, and surface structure but no quantitative measurements of physical properties were made. The deposits on platinum were stripped with nitric acid and analyzed by electrodeposition. The deposits on brass were covered with clear lacquer and preserved as a permanent record of the various experiments.

TABLE I. *Compositions of original and modified solutions*

Component	Solution A	Solution B
NaCN	196.0 g/l	147.0 g/l
CuCN	179.2	150.6
NaOH	10.0	40.0
$NaKC_4H_4O_6 \cdot 4H_2O$	70.5	211.7
$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	9.5	75.9

Experimental Results Obtained with Cyanide-Tartrate Solutions

The compositions of the original solution formulated on the basis of preliminary work not described in this paper and that adopted later are given in Table I. These solutions will be designated hereafter as solution A and solution B, respectively.

The principal objection to solution A was its low lead content since this resulted in considerable concentration polarization. Because of this polarization effect, temperature, current density, and rate of cathode rotation were critical variables.

Information obtained in studies of the effects of sodium hydroxide and of sodium potassium tartrate on electrode potentials and deposit composition led to the development of solution B. This solution contained eight times as much lead (as lead acetate) as did solution A. In spite of this increase, the static lead potential was more negative in solution B than in solution A.

The results obtained in the study of the variables are in most cases presented in graphical form to conserve space. Four curves are shown in all of the graphs except those pertaining to current density and rate of cathode rotation. Three of these are potential curves and include the static potentials of the individual metals measured just before each plating run and the dynamic cathode potential measured during the last minute of each run. The static potentials show the effect of the indicated variable on the concentrations of the copper and lead ions in the solution. The dynamic cathode potentials give the sum of the static alloy potential and the polarization potential. The static alloy potentials have been omitted from the graphs to avoid crowding, but the polarization (dynamic alloy potential minus static alloy potential) is discussed in the text where a significant change was noted. All potentials are relative to the normal hydrogen electrode and, since they are negative to this electrode in every case, the sign of the potential has been omitted.

Each of the curves shown was based on at least five experimental points, well distributed over the range covered. Since the curves were drawn to pass through all of these points, the actual data points used have not been designated.

Solution compositions are indicated by reference to Table I plus a description of any modification made in the solution. The plating conditions, unless otherwise indicated, were as follows: temperature, 40°C; cathode rotation, 1900 rpm (317 ft/min); duration of plating period, 24 min; current density, 30 amp/ft^2 (3.3 amp/dm^2).

The potential measurements and deposit compositions shown in Fig. 3 to 12 were obtained in runs using a platinum cathode surface. Duplicate runs were made using a brass cathode surface. Space does not permit reproduction of photographs of these deposits. However, to present a general idea of the appearance of the deposits and to indicate the improvement resulting from changes in the solution, photographs of deposits obtained under comparable physical plating conditions are shown in Fig. 1 and 2.

Sodium Hydroxide

Five solutions similar to solution A, except that the sodium hydroxide concentrations were 0.0, 10.0, 41.3, 72.3, and 135.0 g/l, were used. The plating conditions were as previously given except that the temperature was 55°C.

The polarization (difference between the potential of the cathode just before and just after opening the plating circuit) decreased from 0.183 volt with no sodium hydroxide to 0.069 volt with 43.0 g/l, but remained nearly constant with further increase in sodium hydroxide concentration.

Fig. 3 shows the effects of increasing sodium hydroxide concentration on the static potentials of copper and lead and on the dynamic cathode po-

tential as measured just before the circuit was opened at the end of each run. The change in the static lead potential to more negative values was probably due to the effect of hydroxyl ions in shifting the equilibrium given below toward the right:

$$Pb^{++} + 4OH^- \rightleftharpoons PbO_2^= + 2H_2O.$$

The effect of sodium hydroxide on the static copper potential is not so readily explained. The initial shift to more negative potentials may have been due to repression by the strong base of the hydrolysis of sodium cyanide, thus increasing the cyanide ion available for complex formation. At higher concentrations, the effect of increasing the sodium hydroxide concentration was to give a less negative copper potential and this suggests the formation of a less stable copper complex.

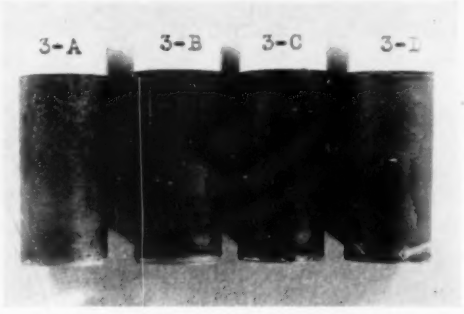

FIG. 1. Deposits from solution A

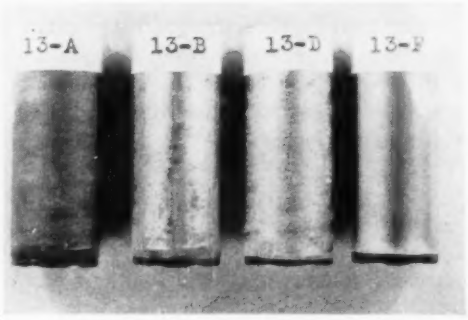

FIG. 2. Deposits from solution B

The dynamic cathode potential (which has been labeled "cathode potential" in the graphs) is nearly constant which means that the decrease in polarization previously mentioned was offset by increasingly negative static alloy potentials corresponding to decreased lead ion concentration.

For the low concentrations of sodium hydroxide, the alloy composition curve shows a minimum which appears to be associated with the minimum in the static copper potential curve. As the two static potential curves diverged, the copper content of the alloy became greater, as is to be expected since copper was the more noble metal in this solution.

Sodium Cyanide

Five modifications of solution A containing 3.0, 3.5, 4.0, 4.5, and 5.0 moles/l of sodium cyanide were prepared and used for runs under the previously described conditions.

The polarization increased from 0.131 volt to 0.323 volt. Of this 0.192 volt increase, 0.180 volt came in the change from 4.0 to 5.0 moles/l where the sodium

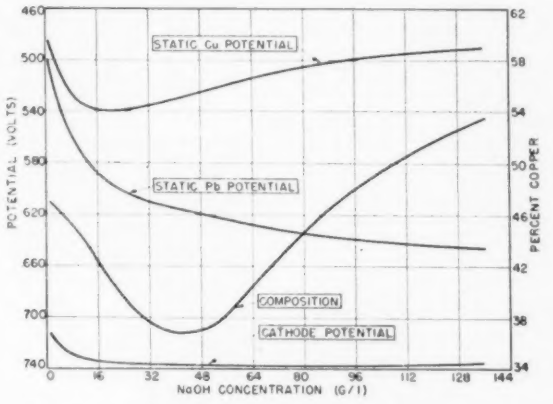

FIG. 3. The effect of sodium hydroxide concentration

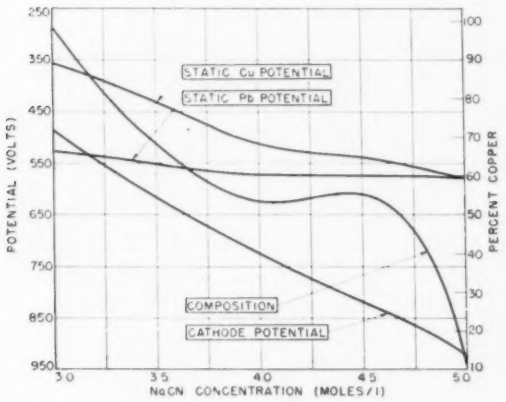

FIG. 4. The effect of sodium cyanide concentration

cyanide was in excess of the theoretical requirement for the formation of the cuprocyanide complex.

Fig. 4 shows the effects of sodium cyanide concentration on the measured potentials and on the composition of the deposits. The static copper potential became more negative as the copper ion was more completely tied up in the cyanide complex. The slight change in the static lead potential was probably due to the effect of sodium cyanide in producing a more alkaline solution through hydrolysis.

The dynamic cathode potential became much more

negative corresponding to more negative static alloy potentials and to increased polarization.

The composition curve shows that cyanide concentration is a critical variable especially above and below the theoretical 2 to 1 ratio of sodium cyanide to cuprous cyanide which roughly corresponds to the nearly flat portion of the curve.

Sodium Potassium Tartrate

Solution A was modified by varying the sodium potassium tartrate concentration to give solutions containing 0.018, 0.125, 0.250, 0.375, and 0.500 mole/l.

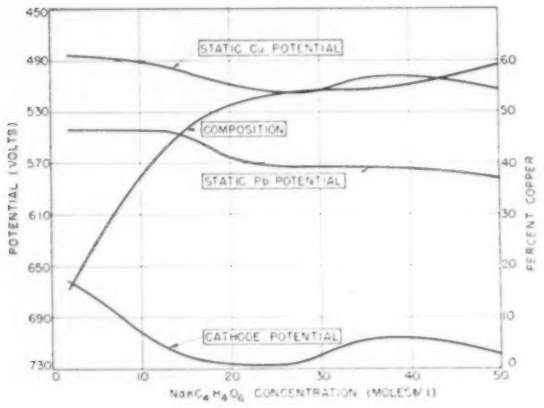

FIG. 5. The effect of sodium potassium tartrate concentration.

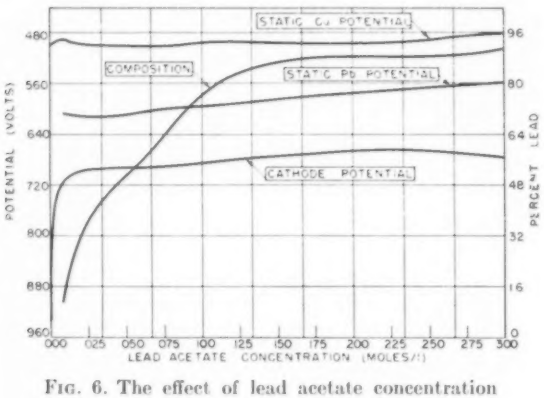

FIG. 6. The effect of lead acetate concentration

The total increase in polarization amounted to 0.036 volt.

The curves given in Fig. 5 show that increasing the tartrate concentration decreases the concentration of lead ion in the solution since the static lead potential becomes more negative. The change in the static copper potential is somewhat similar to that noted with increasing sodium hydroxide concentration (Fig. 3) and may be due to the base produced in the hydrolysis of the tartrate. This could also account for part of the effect in the case of the static lead potential.

The variation on the dynamic cathode potential cannot be readily explained. The initial increase in negative potential was probably due to an increase in polarization but there is no apparent reason for the subsequent shift to more positive values.

No definite relation between the composition curve and the potential curves appears to exist.

Lead Acetate

In order to prepare a series of solutions containing a wide range of lead acetate concentrations, it was necessary to completely change solution A. The changes were as follows: sodium cyanide from 196.0 to 171.5 g/l, cuprous cyanide from 179.2 to 161.3 g/l, sodium hydroxide from 10.0 to 40.0 g/l, and sodium potassium tartrate from 70.5 to 211.7 g/l. Seven solutions were prepared with the lead acetate concentration varied from 0.0 to 0.30 mole/l.

The polarization with no lead acetate in the solution was 0.404 volt. With 0.0075 mole/l of lead acetate, the polarization dropped to 0.196 volt. With further increase in lead acetate concentration, the polarization decreased slowly to a minimum of 0.085 volt.

The curves given in Fig. 6 show that the concentration of lead acetate is not a critical factor above a concentration of 0.15 mole/l.

The alloys obtained in the noncritical range were much lower in copper content than desired but it was later found that the copper content could be increased by adjusting the concentrations of sodium cyanide and cuprous cyanide.

Cuprous Cyanide

The solutions prepared for the study of the effect of cuprous cyanide concentration were modifications of solution B (Table I). These solutions contained 1.30, 1.40, 1.55, 1.60, 1.65, and 1.70 moles/l of cuprous cyanide. The corresponding cyanide ratios, expressed as moles of sodium cyanide per mole of cuprous cyanide are: 2.31, 2.14, 1.93, 1.87, 1.82, and 1.76.

The effect on polarization of increasing the cuprous cyanide concentration was not significant, the extremes being 0.062 and 0.089 volt. This was to be expected since the solutions contained sufficient lead acetate to minimize the concentration polarization which, no doubt, accounted for the high polarization noted in the study of the effect of sodium cyanide concentration. The solution used for the study of the latter variable contained only about $\frac{1}{8}$ as much lead acetate.

Fig. 7 shows the effects of increasing the concentration of cuprous cyanide in solutions having identi-

cal concentrations of sodium cyanide. If these curves were plotted using decreasing concentrations of cuprous cyanide as abscissas they would be fairly similar to those given in Fig. 4, since the variable in each case is actually the ratio of sodium cyanide to cuprous cyanide. However, this apparent duplication of a previous series of runs was made necessary by the considerable modification of solution A resulting from the study of the effect of lead acetate concentration.

A sodium cyanide concentration of 4.0 moles/l in Fig. 4 gives the same cyanide ratio as a cuprous cyanide concentration of 1.5 moles/l in Fig. 7.

The alloy composition curve is seen to be closely related to the curve for the static copper potential. The steep slope of the composition curve indicates that cyanide ratio is a very critical variable.

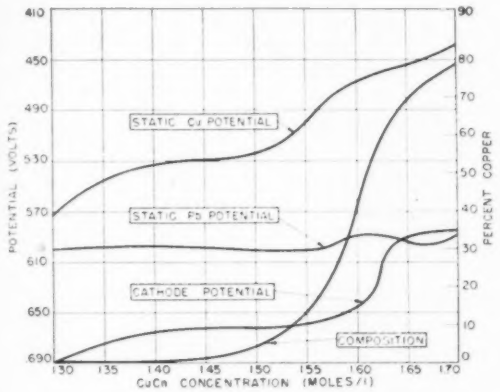

FIG. 7. The effect of copper concentration

Replacement of Sodium Ion by Potassium Ion

A solution containing potassium compounds instead of sodium compounds was prepared and used for electrodeposition in order to determine what effect this replacement has on the deposits, especially on the hardness. It was found to be impossible to prepare a solution using potassium compounds having the concentration of solution B. The solution used was equivalent to a 1–1 dilution of this solution. The usual plating conditions were used except that the temperature was 60°C.

The replacement of sodium ion by potassium ion produced no significant change either in the nature or the composition of the deposit.

Replacement of Tartrate by Citrate

The solution used was equivalent to a 1–1 dilution of solution B except that the sodium potassium tartrate was replaced by an equivalent quantity of sodium citrate and the sodium hydroxide concentration was doubled. The extra sodium hydroxide was necessary to prevent precipitation of lead hydroxide, the citrate appearing to be less effective than the tartrate in holding lead in solution. The usual plating conditions were used except that the temperature was 60°C.

The citrate solution was very similar to a solution of equivalent concentration in which sodium potassium tartrate was used. The potentials, deposit compositions, and characteristics were essentially unchanged by the replacement.

Hydrogen Ion Concentration

Since *p*H is often an important variable in a plating solution, this factor was studied in spite of the very narrow range over which it could be varied. By the addition of acetic acid to solution B, the *p*H was decreased from 13.6 to 13.0. This was the lowest *p*H attainable without causing precipitation. By adding sodium hydroxide, the *p*H was increased to 13.8. These two solutions were compared with solution B after adjusting all three to the same concentration as nearly as possible. The *p*H values were obtained by means of *p*H papers and must be regarded as rough approximations.

The static potentials of copper and lead became more negative as the *p*H was increased but the effect was small in the case of copper. The polariza- was 0.070 volt higher at the lowest *p*H than at the highest. The copper content of the deposits increased by about 27 per cent in going from the lowest to the highest *p*H. The deposit from the low *p*H solution was much inferior to those obtained at the higher values. The *p*H of solution B was about right, and, being very high, was not subject to any significant change during electrolysis or during storage of the solution.

Ammonia

The concentration of ammonia was treated as a variable since the ammonia formed in the aging of some highly alkaline cyanide baths has been observed to produce significant improvement in the deposits obtained. Solutions were prepared by adding 20 ml of concentrated ammonium hydroxide to one 180 ml portion of solution B and 20 ml of water to a similar portion. Since this large addition of ammonium hydroxide produced relatively small changes in the potentials and the deposits, no detailed study of this variable was made.

The effect of the added ammonium hydroxide was to make the static copper potential 0.031 volt more negative and the static lead potential 0.011 volt more negative and to decrease the copper content of the deposits by 17 per cent. Inasmuch as the test solution contained the equivalent of 100 ml of concentrated ammonium hydroxide per liter, it is obvious that any ammonia formed by the breakdown of

the cyanide in the solution would have a negligible effect.

Dilution

To determine the effect of dilution, four dilutions of solution B were prepared and electrolyzed under the usual conditions except that a temperature of 60°C was used.

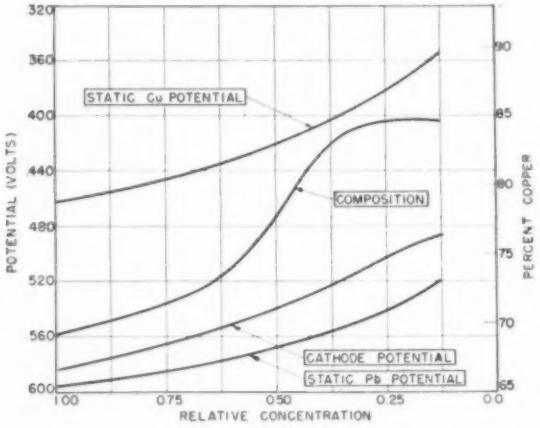

FIG. 8. The effect of dilution

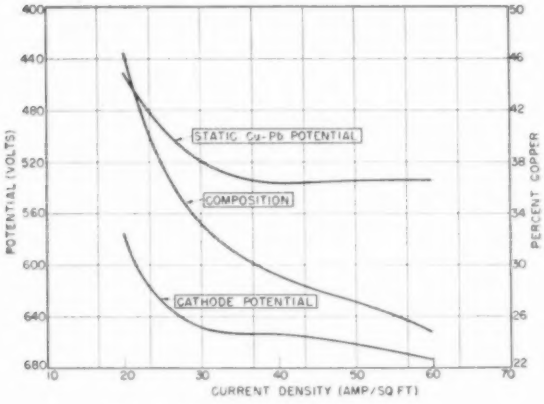

FIG. 9. The effect of current density

The effect of dilution on polarization was negligible. The deposits improved somewhat in appearance with dilution, but the change was not great.

The abscissas in Fig. 8 represent decreasing total concentrations obtained by diluting solution B and the figures indicate relative concentrations based on solution B as unity.

The two static potential curves show a relatively uniform shift to more positive potentials with decreasing total concentration. However, the slopes differ appreciably and the increasing copper content of the deposits with dilution is closely related to the divergence of these curves.

Alloy Anodes

The limited work done indicated that the use of copper-lead alloy anodes is feasible. A more complete study of the anode process is desirable.

Addition Agents

No complete study of the effects of addition agents was made, but 19 such agents (nine metallic salts, eight organic compounds, and two inorganic sulfur compounds) were tried in the hope of reducing the tendency to form nodules. None of these was effective in reducing nodule formation and very few produced any significant brightening of the already relatively bright deposits.

Current Density

The solution used differed slightly from the composition of solution B given in Table I but this would not affect the general trend of the measured potentials and alloy composition with increasing current density.

Using a temperature of 60°C, runs were made at 20, 30, 40, 50, and 60 amp/ft² (2.2, 3.3, 4.4, 5.6, and 6.6 amp/dm²). The plating periods were adjusted according to the current density used so that they were equivalent to the usual 24 minute plating period.

The best looking deposit was obtained at the lowest current density but even at the highest current density the deposit was bright and smooth except for a few fairly large nodules.

The polarization increased by only 0.035 volt over the entire range of current densities, indicating that solution B supplies ions for reduction at the cathode at a satisfactory rate even when a relatively high current density is used.

The changes in cathode potential and copper content of the deposits shown in Fig. 9 are the result of increased polarization with an increase in the current density and are to be expected. The polarization effect is usually greater for the more noble metal except in solutions having a low total concentration of the less noble metal as was true of solution A.

The static alloy potential has been included in Fig. 9, 10, and 11 although this potential is of doubtful significance for an alloy of this type. A portion of the static alloy potential curve does appear to follow the alloy composition curve.

Cathode Rotation

Solution B was used and the temperature was 60°C. Runs were made at cathode rotation rates of 150, 500, 1000, 2000, and 3000 rpm (25, 83, 167, 333, and 500 ft/min).

The smoothest deposit was obtained at the high-

est rate but the deposits with the exception of the one obtained at the lowest speed were very similar in appearance.

Fig. 10 shows that the rate of cathode rotation is not critical above 1000 rpm (167 ft/min). The effect on polarization was not significant as shown by the fact that the curves for the static and dynamic alloy potentials practically parallel each other.

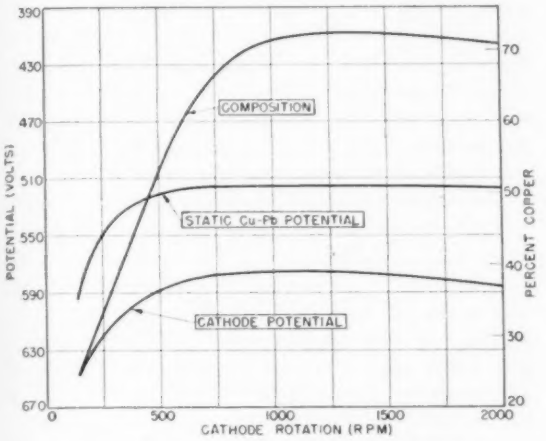

FIG. 10. The effect of rate of cathode rotation

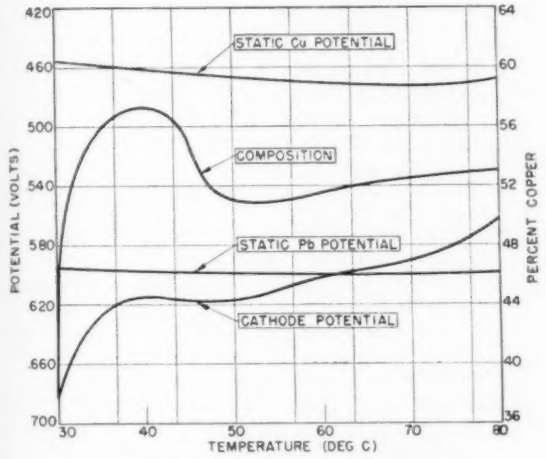

FIG. 11. The effect of temperature

The available information does not furnish an explanation for the fact that the copper content was low and dependent upon rate of rotation at slow speed but practically independent of the rate of rotation at the higher speeds. The effect of agitation on the anode process may well be a factor.

The small decrease in copper content noted at the highest rate of rotation was probably due to an aging effect (to be discussed later) rather than to the increased rate of rotation.

Temperature

Using solution B, runs were made at 30, 40, 50, 60, 70, and 80°C.

The deposits became smoother and brighter with increasing temperature.

A decrease in polarization of 0.034 volt was noted between 30° and 40°C but there was little change with further increase in the temperature.

As indicated by the curves in Fig. 11, the static potentials of copper and lead became somewhat more negative as the temperature was increased. No satisfactory explanation can be offered.

The maximum in the composition curve is due to failure of the copper anode to corrode properly at the lowest temperature used. This resulted in an abnormally low copper content deposit in the first run. On standing in contact with the solution to be used for the second run, the anode film dissolved chemically thus giving the solution a higher copper concentration than it would normally have. During the

TABLE II. *The reproducibility of the potential measurements and the deposit compositions*

Solution compositions:		Plating conditions:
NaCN	147.0 g/l	C.D. 30 amp/ft²
CuCN	150.6	
NaOH	40.0	Temp 60°C
$NaKC_4H_4O_6$	211.7	
$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	75.9	Rotation 1900 rpm

Run No.	1	2	3	4
E_{Cu} (before)	0.459	0.460	0.459	0.459
E_{Cu} (after)	0.457	0.458	0.456	0.456
E_{Pb} (before)	0.595	0.595	0.595	0.596
E_{Pb} (after)	0.596	0.597	0.597	0.597
$E_{cath.}$ (6 min)	0.645	0.644	0.645	0.644
$E_{cath.}$ (12 min)	0.600	0.601	0.599	0.601
$E_{cath.}$ (18 min)	0.593	0.593	0.591	0.591
$E_{cath.}$ (24 min)	0.587	0.587	0.585	0.586
E_{Cu-Pb} (static)	0.512	0.513	0.511	0.510
Polarization	0.075	0.074	0.074	0.076
Per cent copper	72.56	71.13	71.01	70.95

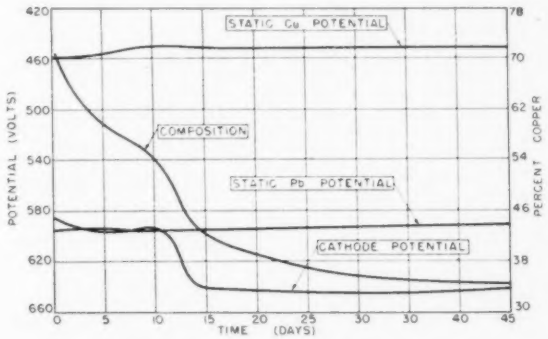

FIG. 12. The effect of aging the plating solution

second run, the anode corroded properly with the result that the deposit had a relatively high copper content. For this reason, as far as the temperature effect at the cathode is concerned, the composition and cathode potential curves in Fig. 11 are significant only in the range 50°–80°C. Since the best deposits are obtained at high rather than at low temperatures, the runs at 30° and 40°C were not repeated. In the range 50°–80°C, the composition of the deposits was nearly constant, indicating that temperature is not a critical variable in this range.

Reproducibility

Using solution B, four successive runs were made under the usual conditions except that the temperature was 60°C.

Table II shows the results obtained. Tables of this type were prepared for each of the factors investigated but have not been included in this paper because of the space required.

As will be evident from Fig. 12, reproducibility of alloy composition such as is shown in Table II is not to be expected for deposits from solutions which have aged for different lengths of time.

Solution Aging

A large portion of solution B was prepared and runs were made over a period of 45 days. The usual plating conditions were employed.

During the 45 day period, the polarization increased by 0.052 volt. In spite of a large change in composition, the deposits changed very little in appearance. The curves shown in Fig. 12 do not offer any clear-cut explanation for the observed aging effect.

The unexpected effect of aging on the composition of the deposits was of sufficient interest to justify a more thorough investigation, and this problem is considered in detail in another paper (11).

Conclusions

1. Of the solutions investigated, the cyanide-tartrate type seems most suitable for the electrodeposition of copper-lead alloys.

2. All possible variables have been studied. Only the ratio of sodium cyanide to cuprous cyanide appears to be critical as far as deposit composition is concerned.

3. Under optimum conditions, bright smooth deposits may be obtained, but these deposits are hard and brittle unless the lead content is relatively high.

4. The plating solution formulated is not stable over a long period of time unless it is stored out of contact with air.

5. The copper-lead alloy plating bath described in this paper is not, in its present stage of development, suitable for commercial use, especially for thick deposits and the higher copper contents.

6. Fundamental information has been obtained which may in the future be useful in developing practical commercial processes.

In most instances the results observed on changing the solution composition or the plating conditions are readily explained and are consistent with well-known generalizations. Some of the results which are characteristic of the type of solution used in this study cannot be explained on the basis of the work done so far but are deserving of more intensive study. Such an intensive study has already been made concerning the aging effect and is reported in another paper (11). Similar studies of other factors are contemplated.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the Journal.

References

1. Q. Marino and The Darlington Wire Mills Ltd., British Pat. 405, 433, Feb. 8, 1934.
2. P. P. Belyaev, A. G. Valeeva, and S. P. Hel'man, *Vestnik Metalloprom.*, **15,** 117 (1935); *Chimie & industrie*, **35,** 855 (1935).
3. P. P. Belyaev, S. P. Markova, and S. P. Hel'man, *Vestnik Metalloprom.*, **16,** 90 (1936); *Chimie & industrie*, **36,** 1161 (1936).
4. W. H. Bagley, B. R. Bagley, and R. W. Berdan, *U. S. Pat.* 2,086,841, July 13, 1937.
5. W. R. Meyer and A. Phillips, *Trans. Electrochem. Soc.*, **73,** 377 (1938).
6. E. S. Roszkowski, H. R. Hanley, W. T. Schrenk, and C. Y. Clayton, *Trans. Electrochem. Soc.*, **80,** 235 (1941).
7. R. Hashimoto, *J. Central Aeronaut. Research Inst.*, No. 2, 116 (1943); *C. A.*, **42,** 1515^b (1948).
8. F. Bollenrath, *Luftfahrt-Forsch.*, **20,** 284 (1943).
9. A. Beerwald and L. Döhler, *Arch. Metallkunde*, **1,** 412 (1947).
10. C. B. F. Young and Clifford Struyk, *Metal Finishing*, **47,** No. 7, 49, 53 (1949).
11. N. W. Hovey, A. Krohn, and A. L. Ferguson, *J. Electrochem. Soc.*, **98,** 155 (1951).

Aging Effects in Copper-Lead Alloy Plating Solutions of the Cyanide-Tartrate Type[1]

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ABSTRACT

Effects of aging in cyanide-tartrate plating solutions for copper-lead alloys were studied during a 50-day period by measurements of single metal potentials, static and dynamic alloy potentials, oxidation-reduction potentials, alloy composition, and absorption spectra of the plating solution. Similar measurements on a portion of the solution stored under nitrogen established atmospheric oxidation as the cause of aging.

INTRODUCTION

During studies of the effects of several variables on the composition and properties of copper-lead alloys deposited from a cyanide-tartrate plating bath, it was reported that an aging effect was observed (1). Over a period of 45 days, the composition of the deposits changed from 71 per cent copper to 35 per cent copper, and the originally almost colorless solution became a deep blue. A possible explanation would appear to involve an oxidation of part of the copper initially present in the univalent state as the colorless cyanide complex to the divalent state, which resulted in the formation of the blue complex with the tartrate present.

The purpose of this investigation was to make a more intensive study of these effects in an attempt to disclose the cause of the aging and to suggest, if possible, a means of overcoming it.

EXPERIMENTAL

A large quantity of the cyanide-tartrate solution was prepared having the composition found by the earlier study to be most suitable:

NaCN	147.0 g/l
CuCN	150.6
NaOH	40.0
$NaKC_4H_4O_6 \cdot 4H_2O$	211.7
$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	75.9

A series of plating runs was made at appropriate time intervals for 50 days, beyond which time the changes produced by aging were no longer significant. To determine whether or not atmospheric oxygen was involved, a part of the solution was stored under nitrogen and an identical series of runs made using this solution. Measurements on this solution were stopped after 25 days since it appeared that further data were unimportant.

The plating equipment was essentially that used for the previous work (1).

All plating was done with a current density of 30 amp/ft^2 (3.3 amp/dm^2) at a temperature of 40°C, with a platinum cathode rotating at 1750 rpm (292 ft/min), and a copper anode. The plating period was 25 minutes.

Before and after each run, the static potentials of copper and lead in the solution were determined. During the plating period, dynamic cathode potentials were measured at 5 minute intervals. The static alloy potential was determined just after the plating current was shut off to make possible a calculation of polarization. The potential of platinum in the solution was measured before and after the plating period to determine any changes in the oxidation-reduction potential of the system.

Each deposit was dissolved off the platinum cup cathode and electroanalyzed for its copper and lead content.

Because of the complexity of the solution, no chemical analyses were made, since it appeared that in so doing, the equilibrium between the various forms of the constituents would be disturbed. Instead, changes in composition of the solution were followed by periodically determining its absorption spectrum using a Beckman quartz spectrophotometer.

[1] Manuscript received June 22, 1950. This paper, prepared for delivery before the Chicago Meeting, October 12 to 15, 1949, abstracted from a thesis presented by Albertine Krohn to the University of Toledo in partial fulfillment of the requirements for the degree of Master of Science.

Discussion of Results

Potential Measurements

The static potentials of copper and lead did not vary greatly throughout the experimental period. In general, they indicate no appreciable variation in the extent to which the copper and lead ions were tied up as a result of complex ion formation.

Measurements made after the plating run showed that the static copper potentials became more positive, indicating that the copper anode had increased the concentration of copper ions in the solution.

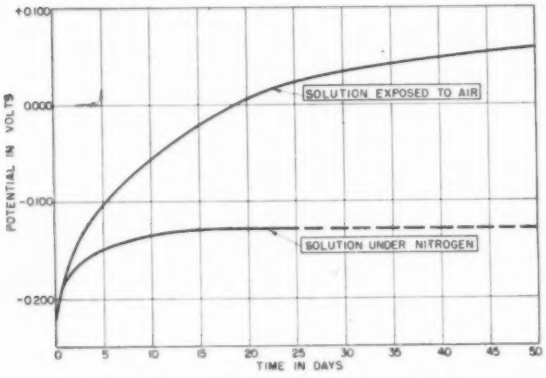

Fig. 1. Oxidation-reduction potentials

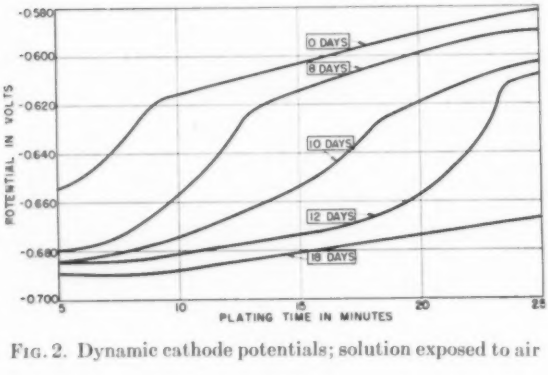

Fig. 2. Dynamic cathode potentials; solution exposed to air

The static lead potentials did not change markedly from their values before the run. Since there was no lead in the anode to replace that plated from the solution, the lead ion concentration apparently was not a critical factor.

The oxidation-reduction potentials definitely were significant as shown by Fig. 1. Assuming that only the cuprous-cupric system is involved, this graph indicates the relative extent of oxidation of the cuprous ion. While it is true that there are other oxidation reactions possible, the correlation between these potentials and the composition changes as indicated by the absorption spectra would seem to warrant this assumption. Oxygen of the air evidently was the important factor since the solution stored under nitrogen showed greatly retarded effects. Some early oxidation did occur because of air dissolved during the preparation of the solution. In any case, the differences in the oxidation-reduction potentials of the two solutions are great enough to indicate that the process is not an auto oxidation-reduction reaction.

Oxidation-reduction potentials measured after the plating period were more negative than those before plating in every case except the run made with the freshly prepared solution. This suggests that during the plating period of the aged solutions, the cupric ion concentration was decreased by reduction to cuprous ions at the cathode. The ratio of cupric to cuprous ions thereby became smaller resulting in a more negative value for the oxidation-reduction potential. Since oxidation was proceeding at a comparatively rapid rate in the freshly prepared solution, the increase in cupric ions due to aging while the initial run was being made apparently more than compensated for the loss due to cathodic reduction. It is assumed here that the amount of copper ion introduced during the plating process was essentially constant for each run.

As would be expected, the difference in the oxidation-reduction potentials before and after the plating increased as the aging process continued. That is, as the cupric/cuprous ion ratio becomes larger because of aging, a relatively greater change in this ratio must occur during the plating period. After the first two days, this difference was small and nearly constant in the solution stored under nitrogen, indicating that the cupric ion concentration was no longer being increased by oxidation.

The cathode potentials measured during the plating process disclose some interesting facts. Fig. 2 shows that the changes in the dynamic potentials were not regular throughout the plating period. During the early runs, the potential showed a rapid increase during the 5–10 minute interval. By the eighth day, the most rapid increment in potential is observed to have occurred during the 10–15 minute period. On the tenth day, it appeared between 15 and 20 minutes and on the twelfth day between 20 and 25 minutes. By the eighteenth day the increase was practically constant during the whole plating period. It is probable that the shift would have been observed in the later runs had the plating period been sufficiently long.

These potential shifts no doubt indicate a corresponding change in the composition of the alloy being deposited. The copper content must increase since the potential becomes more positive. This is substantiated by the fact that the longer the shift

is delayed, the lower is the copper content of the alloy deposited in the 25 minute period. Further evidence of this correlation will be discussed in connection with the composition of the deposits.

A possible explanation for these phenomena may be that, under the conditions of the experiment, the reduction of cupric to cuprous ions at the cathode takes precedence over the reduction of cuprous ions to the free metal. The more the cupric ion concentration was increased by air oxidation, the longer the normal plating of copper was delayed. It must also be borne in mind that, assuming equal efficiencies, twice as much electricity is required to deposit copper from the cupric state as from the cuprous state.

Fig. 3 shows that similar shifts in potential were not observed in the solution stored under nitrogen.

Polarization is doubtless another important factor. Because of the tendency for the static alloy potential to drift, polarization data obtained at the end of the plating periods were not regular. However, polarization did increase from −0.074 volt to −0.149 volt as the solution aged. It remained smaller and more nearly constant in the solution under nitrogen.

Composition of the Deposits

The pronounced changes in composition of the alloy deposited are the most disturbing manifestations resulting from the aging process. Fig. 4 shows that in alloys deposited from the air-exposed solution, the copper content dropped almost 10 per cent after the first two days of aging. The decrease then became less rapid, amounting to less than 2 per cent for each of the next two-day intervals. During the following three runs, the copper content dropped about 8 per cent each time. The rate of decrease then gradually became less until the composition remained nearly constant at about 30 per cent copper for the duration of the experimental period.

In contrast, Fig. 5 shows that the deposits from the solution kept under nitrogen changed only slightly during the first ten days, then remained practically constant at about 4 per cent below its original value. The slight variations during the first ten days may have resulted from slight changes in the time during which the solution was exposed to air before and during the plating operation. The equipment available did not permit the plating to be carried out in an inert atmosphere. However, it should be noted that the deposit from this solution, when it became constant after about ten days, was higher in copper than that obtained after only two days from the solution exposed to air.

As shown in Fig. 2, there is a rather abrupt change in the rate of increase of cathode potential as plating progressed, and this change occurs at a later time in the plating period as the aging period increased. Each time the abrupt change in potential shifted to a later time interval, the copper content of the deposits was decreased by about 8 per cent. After the eighteenth day when the potential shifts no longer appeared, the change in composition practically disappeared.

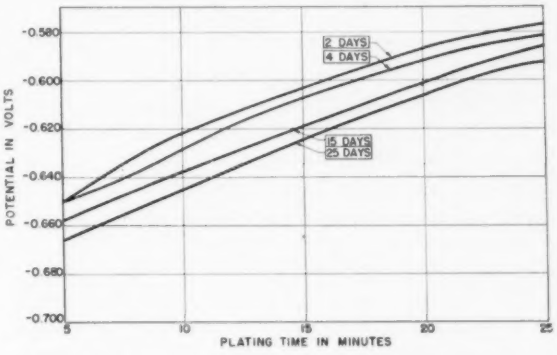

FIG. 3. Dynamic cathode potentials; solution under nitrogen.

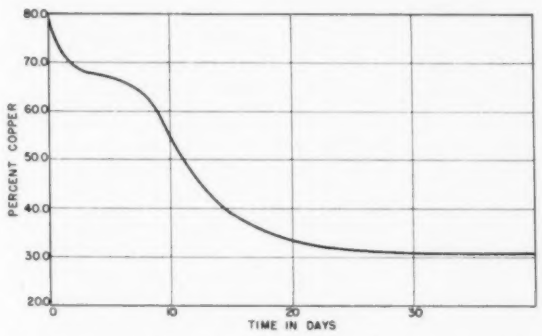

FIG. 4. Composition of the deposits; solution exposed to air

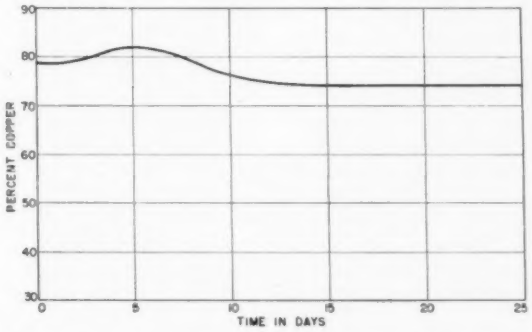

FIG. 5. Composition of the deposits; solution under nitrogen.

Fig. 6 indicates how closely the potential increase occurring in the 5–10 minute plating interval is related to the composition of the deposit. If the increase in potential during this interval and the percentage of copper for the same run are plotted against

the aging period, the two curves are very similar. The few potential values which do not exactly parallel the other curve would do so if corrected within the limit of experimental error. That is, these points are less than 5 millivolts off the curve.

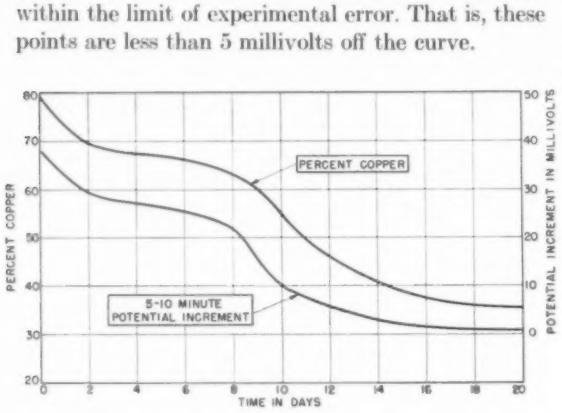

FIG. 6. Correlation of composition with cathode potentials

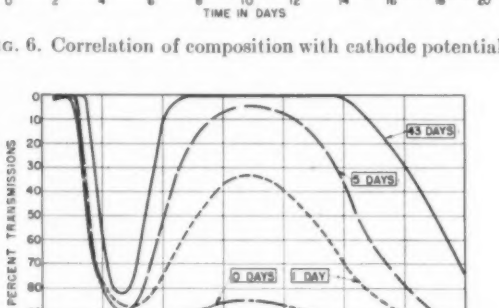

FIG. 7. Absorption spectra; solution exposed to air

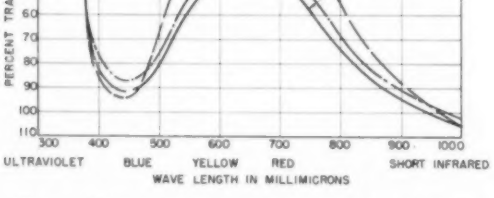

FIG. 8. Absorption spectra; solution under nitrogen

Absorption Spectra

The cuprocyanide complex is colorless and its absorption bands are in the ultraviolet below the range of the spectrophotometer used in this study. However, all cupric solutions have absorption bands in the yellow and red, the width and position of which vary with the nature of the compound, the concentration, and the solvent employed. Organic cupric complexes also exhibit bands in the ultraviolet, the position depending upon the organic radical. The visible color of the compound depends on the narrow region of transmission between the two absorption bands.

For the copper tartrate complex, the absorption is known to begin at about 480 mμ and reaches a maximum at 630 mμ (2). Therefore, a study of the spectrum in this region should serve not only to indicate the presence of the tartrate complex but also to measure its relative concentration as the solution aged.

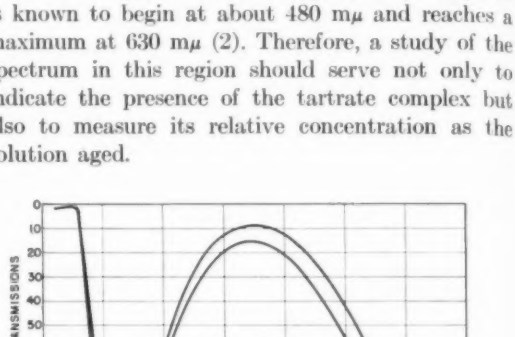

FIG. 9. Comparison of absorption spectra

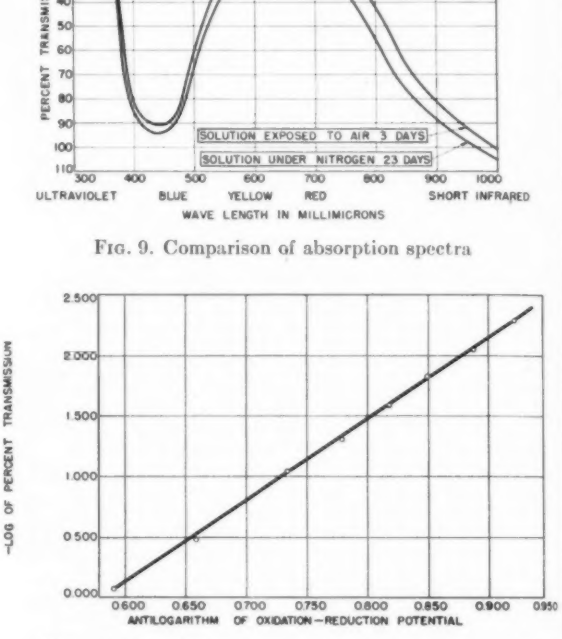

FIG. 10. Correlation between oxidation-reduction potentials and absorption spectra.

Fig. 7 clearly illustrates the increase in the concentration of the blue complex as the aging progressed. The initial measurement made one half hour after preparation of the solution shows very little absorption in the critical region. The solution had only a slight blue-green tinge at that time. In one day, the absorption at 630 mμ increased almost 52 per cent and the solution assumed its characteristic blue color. The large increase in absorption at this point is to be expected since a comparatively small concentration of a highly colored material markedly affects the spectrum. As oxidation progressed, the intensity and width of the absorption band increased until at 43 days the absorption was essentially com-

plete throughout the entire range from green to the red edge of the visible.

Fig. 8 shows spectra obtained from the solution stored under nitrogen. On the first day, the absorption was almost as great as for the other solution. On the third and fifth days, the absorption decreased somewhat, thereafter increasing slightly. This has a rather definite correlation with the composition of the deposits obtained from this solution, since Fig. 5 shows that the percentages of copper increased for these same runs. These deviations, therefore, are real but unexplained.

A comparison of the degree of oxidation of the two solutions is illustrated by Fig. 9. After 23 days, the absorption by the solution stored under nitrogen is less than that of the air-exposed solution on the third day. This is in agreement with the previous data, all of which indicate that oxidation in the solution in the inert atmosphere never progressed beyond the extent of oxidation evident in the air-exposed solution at three days.

If the solution obeys Beer's law, a straight line should be found when the logarithm of the transmittancy at some given wavelength is plotted against the concentration of the cupric complex. If previous assumptions were warranted, the oxidation-reduction potential should be a logarithmic function of the concentration of the cupric ion. Therefore, the antilog of this potential is proportional to the cupric concentration, and a straight line should also be obtained by plotting the log of the per cent transmittancy against the antilog of the oxidation-reduction potential for the same day. The transmission at 640 mμ was selected for this purpose since the greatest sensitivity is found in the region of maximum absorption. Fig. 10 shows that a straight line is obtained by plotting the data in the manner described, thus confirming the assumed relationship between cupric ion concentration, oxidation-reduction potentials, and absorption spectra.

Conclusions

Because of the inconstancy of composition which results from aging, the present plating solution might not be satisfactory for a commercial process. However, the potential measurements suggests that, in a continuous plating process, the copper would be kept in the reduced state so that no great change in composition would be encountered.

It is also possible that by diluting the solution and adding more free cyanide, the aging effects could be minimized or completely eliminated. Dilution increases the difference between the static potentials of copper and lead, resulting in deposits of higher copper content. This could be counterbalanced by the addition of more cyanide. Excess cyanide, because of its reducing properties and also because of the common-ion effect which it exerts on the dissociation of the cuprocyanide complex, might very well be instrumental in the prevention of air oxidation. Further investigation along this line is being conducted.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the Journal.

References

1. A. L. Ferguson and N. W. Hovey, *J. Electrochem. Soc.*, **98**, 146 (1951).
2. P. A. Kober and A. B. Haw, *J. Am. Chem. Soc.*, **38**, 457 (1916).

Effect of Chromium on the Oxidation Resistance of Titanium Carbide[1]

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ABSTRACT

It has been found that a small percentage of chromium in recrystallized titanium carbide improves the resistance of this material to oxidation at elevated temperatures. The amount of oxidation was determined by the increase in weight of specimens of different chromium content after heating in air at 650°, 850°, 1200°, and 1400°C. The data obtained from these tests show that the maximum oxidation resistance, at each temperature, is obtained with an addition of 5 per cent chromium.

Introduction

Recent advances in jet-propelled and turbo-jet engines have placed great emphasis on the need for materials applicable for use at high temperatures. The most important criteria for the successful application of a material at elevated temperatures are: (*a*) strength, (*b*) stability, and (*c*) toughness, all at the temperature of service. In the case of jet engines, erosion as well as abrasion resistance is also very important as the gas velocity in the nozzle has been estimated at 1500 miles per second. In addition, the strength-weight ratio is very important. The most interesting group of promising materials for this purpose are the hard compounds usually formed by powder metallurgical processes. One of these is titanium carbide which, since it is extremely hard (9 on Mohs hardness scale) and refractory (melting point—3140°C), might be expected to have good elevated temperature properties. It is known (1) that Group IV carbides, Ti and Si, are quite stable against oxidation by air at high temperatures, that stability against attack is less for the carbides of Group V elements (Ta, Cb, and V), and that carbides of Group VI (W and Mo) are readily oxidized. It has also been pointed out that Ti and V carbides undergo little or no decomposition below their melting point (2) although some authors have reported the decomposition of titanium carbide in the presence of oxygen at 2100°F (3). Cb and Ta carbides are partially decomposed by heating below their melting point. In some recent work, titanium carbide showed greater resistance to oxidation at 1100°C than either zirconium or vanadium carbide. Along with these properties, titanium carbide, when properly bonded by recrystallization, has high hardness and, consequently, high wear resistance.

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Titanium forms only one carbide consisting of equal proportions of titanium and carbon, one atom of carbon to one atom of titanium in a sodium chloride type lattice. Some have expressed the belief that two atoms of carbon can unite with one atom of titanium to form TiC_2 but there is considerable doubt as to the existence of such a compound (4). The carbide can be produced, however, with a large deficiency of carbon but such a material still retains the titanium carbide structure. Commercially titanium carbide is manufactured (5, 6) from a mixture of TiO_2 and carbon subjected to a temperature of approximately 2000°C or higher in a reducing atmosphere according to the following equation: $TiO_2 + 3C \rightarrow TiC + 2CO$. The titanium carbide used commercially does not, as a rule, contain more than 18 per cent fixed carbon as compared to a theoretical content of 20 per cent. In order to arrive at a content of 18 per cent, however, an excess of carbon is required which in the analysis of the finished product is found in the form of graphite since the excess carbon crystallizes out on cooling (7). The amount of free carbon which the carbide contains may be controlled by the heating and, more particularly, the cooling rate used in the manufacture of the carbide as well as by the temperature at which the carbide is produced. The higher the solubility of carbon in the titanium carbide, which solubility increases with temperature, the greater the amount of free carbon formed on cooling. The chief use for titanium carbide is in sintered carbide cutting-tool materials and the majority of such users desire a carbide low in free carbon because of the adverse effects of this carbon on the properties. The effects of free carbon in titaniun carbide when used alone are not too well established. A process has been developed (8) which greatly reduces the free carbon through the addition of Cr_2O_3 to the TiO_2 plus C mix. On further investigation in this laboratory, it was found that a small percentage of chromium, added as Cr_2O_3, in

the titanium carbide improves the resistance of this material to oxidation and also produces larger crystals as well as giving a cleaner, more metallic fracture. Additional oxidation tests have now been made on titanium carbide with chromium to determine to what extent the oxidation resistance could be increased and also the amount of chromium necessary for maximum oxidation resistance.

Commercial cemented carbides have generally been made with the use of an auxiliary or binder metal to cement together the finely divided carbide particles. These binder metals serve not only as a cement for a mechanical bond but also as a solvent for the carbides so that the carbide particles may merge and form a continuous mass (9). Therefore, the two main requirements for a binder metal (10) are: (*a*) it must be a metal in which the carbide is soluble in reasonably high percentages at the sintering temperature, and (*b*) the metal must have no affinity for carbon, so as not to decompose the carbide. Chromium, since it is a fairly strong carbide former, does not fulfill the requirement of a binder metal and, therefore, should not be considered as one.

Experimental Procedure

Experimental data were obtained by heating samples of titanium carbide containing varying percentages of chromium in air for known periods of time at controlled temperatures. The gain in weight of the specimens after a given duration of exposure was used for measuring the resistance of the material to attack by the oxidizing atmosphere. The specimens used in this determination were in the form of one inch discs approximately one-eighth inch thick. The chromium, calculated as weight percentage of the materials added, was incorporated in the titanium carbide as green chromic oxide (Cr_2O_3) so that the discs contained the following percentages of chromium: 0, 0.5, 1.0, 2.0, 4, 6, 10, and 20 per cent. After mixing the two powders and adding a volatile organic binder, discs were compacted in a one inch mold using 5000 psi. After drying, the green discs were packed in a graphite crucible with arc furnace TiC ($-10 + 40$ mesh) so that a reducing atmosphere would be maintained and then heated in an induction furnace to approximately 2210°C for 25 to 30 minutes to recrystallize the titanium carbide. The original titanium carbide contained 18.69 per cent combined carbon and 0.76 per cent free carbon.

Following the recrystallization, the discs were subjected to oxidation tests in which they were heated in a muffle furnace for one hour at each of the following temperatures: 650°, 850°, 1200°, and 1400°C. Each specimen was placed in a small boat so that the errors incurred by spalling of the oxide, either at temperature or during cooling, could be avoided. The furnace was not airtight and during the heating the observation peephole in the furnace door was left open to permit a free access of air to the specimens. The specimens were removed from the furnace and cooled in air.

During the recrystallization of those discs containing the 10 and 20 per cent chromium additions, the specimens fused together, making it necessary to powder the material after heating, then repress and recrystallize a second time to obtain satisfactory specimens. The high temperature used in recrystallizing the titanium carbide resulted in a reduction of the chromium content especially in those discs, mentioned above, which were recrystallized a second time. For this reason, the specimens could not be designated by the chromium added to the original mixture but rather by the analysis after recrystallization, prior to the oxidation tests. Results of these analyses are as follows:

Chromium added	2.0	4.0	6.0	10.00	20.00
Chromium remaining	2.11	3.80	5.02	4.04	5.95

These figures show the large loss of chromium incurred during the recrystallization of the 10 and 20 per cent discs and that with lower chromium additions the loss was much less. At least a part of this difference could be due to the double heat treatment and, therefore, longer time at temperature that was necessary to obtain satisfactory specimens with the higher chromium additions. Therefore, the specimens containing the lower percentages of chromium are designated according to the amounts added, since the change in chromium content was very small. Those discs with larger chromium contents will be designated according to chemical analysis. Thus the percentages of chromium referred to in this report will be the actual amount remaining in the sample after recrystallization prior to the oxidation tests.

Results

The data obtained from the oxidation tests are listed in Table I which gives the density, weight increase, and per cent oxidation of each disc tested at each of the four testing temperatures. The series at each testing temperature showed the same general trend and this is best shown by Fig. 1—a plot of per cent increase in weight vs. per cent chromium for each temperature. As seen in Table I, the second recrystallization had undoubtedly caused an excessive loss of chromium but, aside from this, it had a noticeable effect on the oxidation resistance of the titanium carbide. When compared to the other discs, recrystallized once, the results were somewhat anomalous. Because of the fact that only those discs

TABLE I. *Results of oxidation tests on titanium carbide with various amounts of chromium*

% Cr		Density before oxidation	Weight (g)		Weight increase	
Added	Retained		Before oxidation	After oxidation	g	%
			Tested at 650°C			
0.0	0.0	3.60	9.632	9.946	0.313	3.25
0.5	0.5	3.66	9.236	9.509	0.273	2.96
1.0	1.0	3.70	9.465	9.820	0.355	3.75
2.0	2.1	3.71	9.390	9.685	0.295	3.14
4.0	3.80	3.93	9.477	9.635	0.158	1.67
6.0	5.02	4.03	9.207	9.305	0.098	1.06
10.0	4.04	3.93	9.292	9.372	0.080	0.86
20.0	5.95	3.74	8.241	8.347	0.106	1.31
			Tested at 850°C			
0.0	0.0	3.64	9.476	9.584	0.108	1.14
0.5	0.5	3.76	9.211	9.312	0.101	1.10
1.0	1.0	3.69	9.339	9.461	0.122	1.31
2.0	2.1	3.72	9.396	9.491	0.095	1.01
4.0	3.80	3.78	9.291	9.369	0.078	0.84
6.0	5.02	4.07	9.338	9.391	0.053	0.57
10.0	4.04	3.86	8.971	9.125	0.154	1.72
20.0	5.95	3.82	8.404	8.553	0.149	1.77
			Tested at 1200°C			
0.0	0.0	3.66	9.564	9.831	0.267	2.80
0.5	0.5	3.69	9.236	9.492	0.256	2.81
1.0	1.0	3.70	9.482	9.805	0.323	3.41
2.0	2.1	3.66	9.442	9.698	0.256	2.71
4.0	3.80	4.02	9.338	9.570	0.232	2.49
6.0	5.02	4.10	9.388	9.592	0.204	2.17
10.0	4.04	4.00	9.262	9.532	0.270	2.92
20.0	5.95	3.88	7.808	8.132	0.324	4.02
			Tested at 1400°C			
0.0	0.0	3.55	9.364	9.691	0.327	3.50
0.5	0.5	3.67	9.185	9.550	0.365	3.98
1.0	1.0	3.65	9.583	10.098	0.515	5.37
2.0	2.1	3.75	9.454	9.760	0.306	3.24
4.0	3.80	4.02	9.317	9.568	0.268	2.88
6.0	5.02	4.12	9.232	9.502	0.270	2.93
10.0	4.04	3.90	9.077	9.436	0.359	3.96
20.0	5.95	3.82	8.429	8.770	0.341	4.05

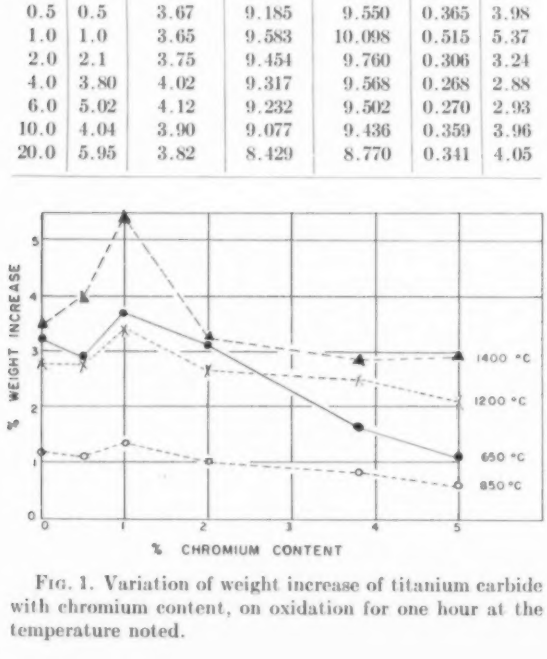

FIG. 1. Variation of weight increase of titanium carbide with chromium content, on oxidation for one hour at the temperature noted.

which originally contained 10 and 20 per cent Cr were recrystallized twice, it was decided that this discrepancy in specimen preparation would invalidate any comparison and that the results obtained on those samples should be disregarded. These results appear in the tables but to avoid confusion have not been plotted.

As would be expected, lowering the temperature produced a decrease in the amount of oxidation with the exception of the series heated at 650°C. This is shown in Fig. 2, where the weight increase is plotted against temperature for each chromium content. The amount of oxidation obtained at the lower temperature was greater than that obtained at 850°C in all instances, and comparable to that obtained at the higher temperatures in most of the specimens with less than 3 per cent chromium. It was first thought that this increase was due to a difference

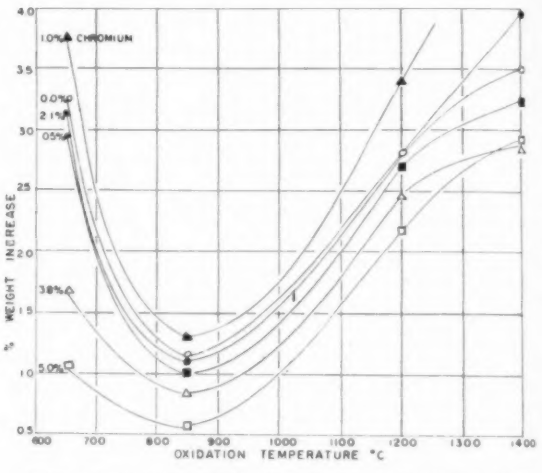

FIG. 2. Variation of weight increase of titanium carbide containing the noted amounts of chromium with temperature of oxidation for 1-hr periods.

in air supply in the furnace during the one test. However, rechecks of each series under constant conditions of time, temperature, and air supply showed values nearly identical with those obtained in the first tests.

Furthermore, the effects of increased air supply were determined by heating a series of samples at 850°C, maintaining a steady stream of air flowing over the specimens. The results of this test agree very well with the results of the previous run at the same temperature with only the peephole of the furnace open. With the exception of the 1 per cent Cr sample, in which a decrease of 0.23 per cent was noted, the values varied by less than one tenth of a per cent. From this, it is evident that a slight flow of air during the oxidation heating has little or no effect on the amount of oxidation that takes place during a given period of time at a specified tempera-

ture. However, greater velocities of air may produce different results.

There are two effects of oxidizing a carbide which make interpretation of the weight increase somewhat difficult. These are: (*a*) pickup of oxygen from the atmosphere by the metal, and (*b*) loss of carbon through oxidation. The first of these would bring about an increase in weight while the second would cause a loss of weight. This would mean that the measured increase in weight does not represent the total amount of oxygen absorbed from the atmosphere but rather the difference between the two effects mentioned above. To determine the influence of this carbon loss, samples were analyzed both before and after the oxidation tests. As would be expected, the loss of carbon was greatest at the higher temperatures. Correction for this, adding the carbon loss to the increase in weight, would indicate the true increase in weight or the total weight of oxygen absorbed from the atmosphere. A calculation of corrected weight changes for the 5 per cent Cr samples is presented in Table II.

Since the oxidation of carbon increases with temperature, the results for each sample obtained at a given temperature should be corrected in the above manner. This correction factor would vary with the amount of carbon oxidation and therefore with temperature. Consequently, a larger weight increase would result at each temperature with the difference becoming greater at the higher temperatures. In effect, this would raise each curve but would not alter the shape or relative position.

On macroscopic examination all discs, with the exception of those of straight titanium carbide, appeared to be well recrystallized and had a silvery gray to a silvery white fracture. The straight titanium carbide discs were fine-grained but had a gray, nonmetallic fracture. Those discs which were oxidized the least showed no "scale" that could be separated from the sample. Only with the higher amounts of oxidation did an actual scale appear and then in some cases four separate layers could be observed. These were: (*a*) dark glazed scale on the outside with a metallic sheen, (*b*) gray layer, (*c*) orange layer, and (*d*) fine yellow powder or ash which covered the recrystallized titanium carbide core. X-ray analysis of the two most prominent layers (the glazed surface scale and the yellow powder) showed both to have the structure of TiO_2 (rutile). The oxide scale of those discs which contained 5 per cent Cr showed approximately 5 per cent chromic oxide. As would be expected, the scale thickness increased with the weight increase. The color of the outer oxide scale indicates a deficiency of oxygen which could be due to the deoxidizing effect of the carbon lost during oxidation. Visual examination of the scale showed the following correlation with increasing chromium: (*a*) a decrease in the amount of yellow powder or ash formed over the titanium core, and (*b*) the formation of a thinner, lighter, and more adherent scale.

It may be observed from Table I that increasing density of the discs coincides with decreased oxidation. From this it can be concluded that the decrease in oxidation may have been due to the decrease in porosity, or greater density, of the higher chromium discs. Therefore, the pressure used in molding the discs may be an important variable. To determine the importance of this deduction, three samples were tested. These were:

1. A sample from a recrystallized titanium carbide bar that had been formed simply by tamping the powdered TiC in a paper mold with practically zero pressure, and then heating in a carbon resistance furnace to a temperature of 2010° to 2490°C and holding for approximately three hours.

2. Straight titanium carbide disc molded under 5000 psi, then recrystallized at 2210°C for ½ hour.

3. Titanium carbide disc containing 5 per cent Cr molded and recrystallized in the same manner as sample 2.

Sample 1 was approximately the same size as the testing discs since a change in surface to volume relationship would result in different data, especially in the oxidation tests. The results obtained from tests on the three samples mentioned above are shown in Table III.

The difference in absorption and density between samples 1 and 2 is probably due to the higher tem-

TABLE II. *Effect of carbon loss*

Temperature of oxidation	650°C	850°C	1200°C	1400°C
% Total carbon—after recrystallization	16.04	16.04	16.04	16.04
% Total carbon—after oxidation	15.81	15.93	15.20	13.87
Weight prior to oxidation—g	9.207	9.338	9.388	9.232
Weight after oxidation—g	9.305	9.391	9.592	9.502
Weight difference	0.098	0.053	0.204	0.270
Weight loss of carbon	0.020	0.009	0.080	0.20
Corrected weight difference	0.118	0.062	0.284	0.470

TABLE III. *Effect of molding pressure and density on oxidation*

Sample	Cr, %	Molding pressure, psi	Density, g/cm³	Absorption, %	% Oxidation (850°C) 1 hr, %
1	0	0	4.18	2.8	1.11
2	0	5000	3.64	5.5	1.14
3	5	5000	4.07	4.0	0.57

perature or longer soaking period used in recrystallizing sample 1. This indicates that the density of the discs is not a function of the pressure applied in shaping but rather of the temperature and time of recrystallization. Oxidation results on these samples show that the effect of density on resistance to oxidation is practically negligible. The results of the oxidation test on sample 3 show that chromium reduces the oxidation of titanium carbide not merely by bringing about a higher density on recrystallization, but chiefly through the influence of the chromium, *per se*.

To determine the nature of the reaction between Cr_2O_3 and TiC during the recrystallization, chemical analyses as well as x-ray patterns of the discs were obtained. The x-ray patterns obtained from the 5.02 and 5.95 per cent Cr discs showed titanium carbide with an indication of TiO_2 being present in the second sample. However, the peaks of the titanium carbide pattern were displaced indicating a change in lattice parameter. This change may be due to a substance in solid solution with the titanium carbide. The results of chemical analysis of these same discs are tabulated in Table IV. On recrystallizing, there was a weight loss of approximately 2 per cent on the 6 per cent Cr disc and 9.5 per cent on the 20 per cent Cr disc.

TABLE IV. *Effect of recrystallization on chemical analysis*

	Original TiC	6% Cr disc		20% Cr disc	
		Before	After	Before	After (2nd)
		Recrystallization		Recrystallization	
% Free C	0.76	0.69	0.10	0.54	0.31
% Total C	18.69	17.02	16.04	13.20	12.42
% Chromium	0.0	6.0	5.02	20.00	5.95

Discussion

These results indicate that chromium has a definite effect on the oxidation resistance of titanium carbide. The addition of a small percentage of chromium (0.5 and 1.0%) lessened the resistance to oxidation, as indicated by a larger weight increase. However, further increasing the amount of chromium increased the resistance until a maximum was reached at 5 per cent Cr. The amount of oxidation with this chromium content was considerably below that obtained on straight titanium carbide: e.g., one hour at 650°C produced a weight increase of 3.25 per cent on straight titanium carbide while the addition of 5 per cent Cr reduced this value to 1.06 per cent. This same trend was observed at each of the testing temperatures.

It is known that chromic oxide is decomposed by carbon, the reaction beginning at 1180°C (11). It is also known that Cr_2O_3 can be reduced by titanium carbide even though chromic oxide belongs to the group of difficultly reducible oxides (12). During the recrystallization of titanium carbide containing chromic oxide, therefore, the Cr_2O_3 may react with either or both the free and the combined carbon to form a chromium carbide. There are three known stable carbides in the chromium-carbon system (13): Cr_3C_2, orthorhombic in structure; Cr_7C_3, which is trigonal; and Cr_4C, the only cubic carbide. In the study of high temperature alloys, this latter carbide has been identified as $Cr_{23}C_6$.

The formation of solid solutions of various carbides in each other, analogous to alloying in metals, has been known for some years (14). More recent work (15) has shown that the solubility of various carbides in one another is greatly dependent upon differences in atomic diameters—or the nearest approach of atoms in the carbide lattice—as well as upon similarity of structure. Cr_4C could be soluble in TiC on the basis of structure alone since both are cubic; however, the vast difference in size (lattice parameter of TiC = 4.32 Å; Cr_4C = 10.6 Å) would indicate practically zero solubility.

The observed size change of the titanium carbide could also be due to chromium dissolved in the carbide as metal rather than the carbide. This chromium could be the result of the decomposition of chromium carbide at the high temperature of recrystallizing treatment. This decomposition of chromium carbide, similar to that of silicon carbide, had been previously noted by Ruff (16). The chromium could enter the titanium carbide lattice, replacing titanium atoms, thus forming a complex carbide similar to orthorhombic cementite (17) $(FeCr)_3C$ found in chromium steels. This could cause a change in lattice parameter but no change in structure. At this point, it may be of interest to note that, in the higher chromium samples, the losses of chromium and carbon are in nearly the exact ratio, 17 to 1, as is found in Cr_4C.

It appears as though the poor oxidation resistance of these samples to which 10 and 20 per cent Cr had been added may be due to the presence of oxides of titanium in the samples. Even though 4–6 per cent Cr remained in the samples after recrystallization, the oxidation resistance was low. As mentioned above, the primary reaction occurs between the Cr_2O_3 and the free carbon in the titanium carbide, but with an excess of Cr_2O_3 present, a second reaction begins. The chromic oxide is reduced by the titanium carbide forming an oxide of titanium which, in all probability, remains in the sample. This would result in a higher oxygen content of the carbide (as has been shown by vacuum fusion analysis) and would also

decrease the oxidation resistance (this result was observed in these experiments). On this basis, a definite relationship would appear to exist between the amount of chromium that should be added and the free carbon which the carbide contains.

In whatever form the chromium is present, it results in improved resistance to oxidation. Oxidation of straight titanium carbide at temperatures over 1000°C produces an oxidation product which offers no further protection to the body. The presence of chromium in the carbide produces the refractory Cr_2O_3 in the scale and this protects the body from further oxidation.

It should be pointed out that this work was done on straight titanium carbide, that is, without the use of an auxiliary or binder metal. The improvements noted can be due only to the presence of the chromium in the carbide. This serves to indicate that the properties of carbides, analogous to those of metals, may be improved through the use of "alloying" elements, and from this could come a series of materials that could be applicable at temperatures above the useful range of most metallic alloys.

Conclusions

1. Chromium added to titanium carbide as Cr_2O_3, prior to recrystallization, affects the oxidation resistance of the carbide in a manner depending on the amount added.

2. Small percentages of chromium (0.5 and 1% Cr calculated as weight per cent of the materials added) decreased the oxidation resistance in a given time at 650° to 1400°C while larger percentages, up to 5 per cent Cr, increased the oxidation resistance.

3. The maximum amount of oxidation resistance occurs with 5 per cent Cr, and the amount of oxidation at a given temperature with this amount of chromium is considerably less than that obtained on straight titanium carbide.

4. In preparing samples for 10 and 20 per cent chromium mixtures, double recrystallization was necessary to obtain satisfactory specimens and, therefore, the amount of oxidation resistance observed in these samples may not be comparable, because of the unknown influence of this difference in the method of preparation of the samples.

5. Chromium in recrystallized titanium carbide probably occurs as a solid solution and not as a binder metal.

6. Other effects of chromium on titanium carbide that were observed in addition to the effect on oxidation resistance were: (*a*) increased density and (*b*) decrease in the amount of free carbon.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the Journal.

References

1. K. Becker, "Hochschmeltzende Hartstoffe," Berlin (1933).
2. E. Friederick and L. Sittig, *Z. anorg. u. allgem. Chem.*, **144,** 169 (1925).
3. C. G. Goetzel, *Iron Age*, **161** (18), 78 (1948).
4. H. J. Goldschmidt, *J. Iron Steel Inst.*, **160,** 345 (1948).
5. G. A. Meerson and Ya. M. Lipkes, *J. Applied Chem. U.S.S.R.*, **14,** 291 (1941).
6. G. Meerson, *Ann. secteur anal. phys.-chim. Inst. chim. gér. U.S.S.R.*, **16,** 197 (1943); *C. A.*, **39,** 4310⁴ (1945).
7. H. Franssen, *Arch. Eisenhüttenw.*, **19,** 79 (1948).
8. C. Laughlin and E. Wainer, U. S. Pat. 2,491,410, Dec. 13, 1949.
9. L. Wyman and F. Kelley, *Am. Inst. Mining Met. Engrs. Tech. Pub.*, No. 345 (Sept. 1930).
10. J. Redmond, *Iron Age*, **159** (5), 42 (1947).
11. J. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, page 182, Longmans, Green & Co., New York (1931).
12. Dawihl, "Hard Metal Alloy Studies," Feb. 11, 1941, PB Report 70489.
13. A. Westgren, *Metal Progress*, **20,** 57 (1931).
14. L. P. Molkov and V. V. Vicker, *Vestnik Metalloprom.*, **16,** 78 (1936).
15. J. Norton and A. Mowry, *Trans. Am. Inst. Mining Met. Engrs.*, **185,** 133 (1949).
16. O. Ruff, *Z. Elektrochem.*, **24,** 157 (1918).
17. E. C. Bain, "Functions of the Alloying Elements in Steel," Published by American Society for Metals, New York (1939).
18. J. Redmond and E. Smith, *Trans. Am. Inst. Mining Met. Engrs.*, **185,** 987 (1949).

The Borides of Some Transition Elements[1]

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ABSTRACT

The crystal structure work on the borides of the transition elements is summarized. It is shown that the borides may be classified according to the boron arrangement. The phases are regarded as metal lattices with boron in the interstices. The boron atoms form an increasing number of boron-boron contacts with increasing boron content of the intermediary phases of a system, from isolated boron atoms to a three-dimensional boron network.

The borides are in many ways related to the hydrides, nitrides, and carbides but the presence of boron-boron bonds modifies the picture. An attempt to apply Pauling's theory of the metallic state on these compounds has not been successful.

INTRODUCTION

Since 1945 the borides of the transition elements have been studied at the Institute of Chemistry of the University of Uppsala, Sweden. A number of binary systems between transition elements and boron have been investigated and the results show that these borides have metallic properties. They are often very hard and inert, with high melting points. A survey of the structures formed may be of interest for a possible technical use of the borides. Much of the present paper may be found in more detail in an earlier publication (1).

The borides have been prepared by sintering or melting mixtures of metal and boron together either in evacuated silica tubes at 1100°–1200°C or in vacuum furnaces at 1200°–2000°C. Starting materials have been transition metals and boron, the boron being prepared by vapor phase reduction of boron tribromide with hydrogen in silica tubes. The alloys have been investigated mainly by means of x-ray methods. The position of the boron has been determined by space considerations or, in some alloys of light metals, by electron density projections.

STRUCTURES OF THE INTERMEDIARY BORIDE PHASES

The boron atoms have a general tendency to form chains, nets, or three-dimensional frameworks through the metal lattice with increasing boron content of the systems. The structures are most conveniently discussed on the basis of the boron arrangement. Some structure determinations on borides, reported by other investigators, are included in the following discussion. The structures hitherto found are summarized in Table I, together with references.

Borides with isolated boron atoms.—To this group belong a great number of borides of the $CuAl_2$-type ($C16$), as well as the closely related δ-phase in the manganese boron system. Both types consist of sheets of tetrahedra of metal atoms with boron atoms in the holes between these sheets (Fig. 1). Geometrically, the boron atoms are arranged in strings through the metal lattice with a boron-boron distance slightly greater than $2r_B$. The string formation may indicate a tendency for boron-boron bond formation also for these phases.

Borides with boron chains.—Three structure types with the boron atoms forming zigzag shaped chains have been observed (Fig. 2). They are closely related, and the metal lattices may be regarded as consisting of trigonal prisms connected in different ways. Channels appear through which boron chains are extended through the lattices.

Borides with double chains (fragments of nets).—In the borides of composition Me_3B_4 the boron atoms form double chains. The double chains may also be regarded as fragments of boron nets, giving these borides an intermediate position between borides with boron chains and borides with boron nets (Fig. 3). The distance between adjacent boron atoms in different halves of a double chain is in the order of magnitude of a double bond, whereas the boron-boron distance in the same halves has the value of a single bond.

Borides with two-dimensional nets.—The next step in the connection of the boron atoms, the formation of hexagonal boron nets (Fig. 4), has been observed for several phases. Most of these borides belong to the AlB_2-type ($C32$). In the molybdenum- and tungsten-boron systems, phases with the ideal composition Me_2B_5 exist, having more complicated structures. The lattices of all these phases are closely related and may be described as consisting of alternating close-packed metal sheets and hexagonal boron nets or slightly puckered boron sheets, formed by nets with additional boron atoms in the centers of some meshes.

[1] Manuscript received June 26, 1950. This paper prepared for delivery before the Cleveland Meeting, April 19 to 22, 1950.

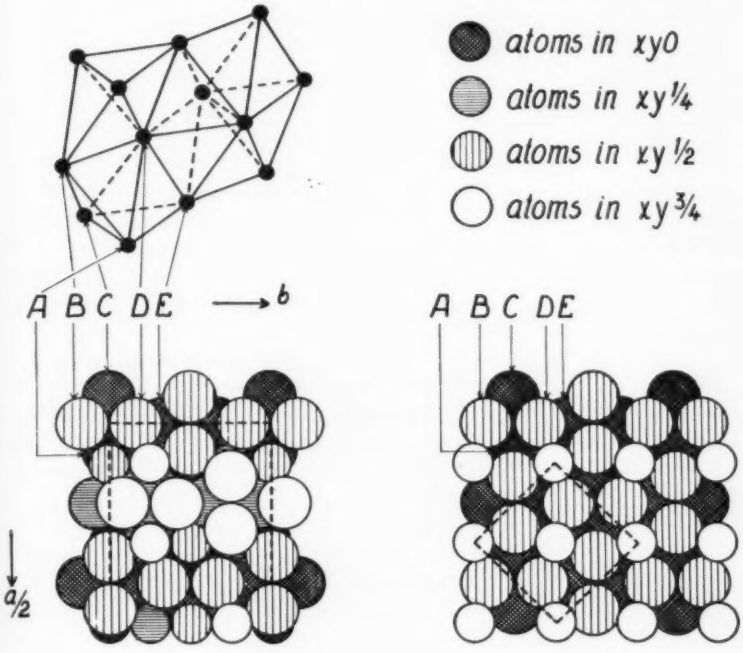

FIG. 1. Borides with isolated boron atoms (large circles represent metal atoms, small circles boron atoms). Left: δ-phase in the Mn-B system. Right: Me_2B-borides of the $CuAl_2$-type.

TABLE I

Boron arrangement	Borides of the transition elements	References No.
Isolated atoms	(*a*) Borides of the $CuAl_2$-type: Mn_2B, Fe_2B, Co_2B, Ni_2B, Mo_2B, Ta_2B, W_2B	2–6
	(*b*) δ-phase in the Mn-B system[+]	2
Zig-zag chains	(*a*) Borides of the CrB-type: CrB, CbB, TaB	6–8
	(*b*) Borides of the FeB-type: MnB, FeB, CoB	2, 4
	(*c*) Borides of the MoB-type: MoB[+], WB[+]	5
Double chains (fragments of nets)	(*a*) Borides of the Ta_3B_4-type: Cr_3B_4, Mn_3B_4, Cb_3B_4, Ta_3B_4.	2, 6, 8
Hexagonal nets	(*a*) Borides of the AlB_2-type: (AlB_2), TiB_2, VB_2[+](?), CrB_2, ZrB_2, CbB_2[+], TaB_2[+].	6–12
	(*b*) ε-phase in the Mo-B and W-B[+](?) systems (not isomorphous but closely related)	5
Three-dimensional frameworks	(*a*) Borides of the CaB_6-type: (CaB_6), (SrB_6), (BaB_6), YB_6, LaB_6, CeB_6, PrB_6, NdB_6, GdB_6, ErB_6, YbB_6, ThB_6.	13–16
	(*b*) Borides of the UB_{12}-type: UB_{12}	17

[+] Extended homogeneity range.

Borides with three-dimensional boron frameworks.—A great number of borides with composition MeB_6 have been reported, the metals including some non-transition elements. The boron atoms of these borides form a three-dimensional framework with the metal atoms in the interstices. Also, UB_{12}, recently reported, is closely related to the borides mentioned with a three-dimensional boron framework. It is of interest to note that the boron atoms of these borides near the boron side of the systems have five boron

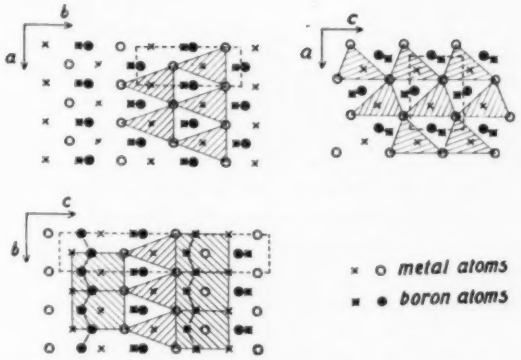

FIG. 2. Projections of boride structures with boron chains (circles and crosses are situated at levels ½ apart). Above left: CrB-type. Below left: MoB-type. Right: FeB-type.

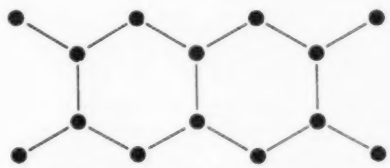

FIG. 3. Double chain of boron atoms

neighbors in contact, thus following Hume-Rothery's (8-N)-rule.

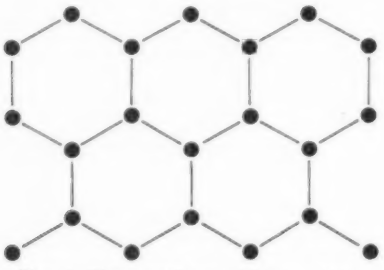

FIG. 4. Hexagonal net of boron atoms

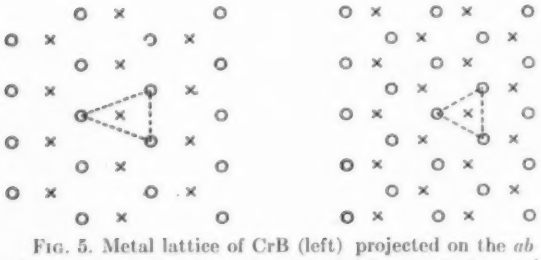

FIG. 5. Metal lattice of CrB (left) projected on the *ab* plane, compared with a hexagonal close-packed metal lattice (right).

GENERAL DISCUSSION

The Existence of Boron-Boron Bonds

The general tendency for the boron atoms to form boron-boron contacts may be only a consequence of a convenient space arrangement of the atoms, or it may involve boron-boron bonds. The experimental evidence clearly shows that the contacts are of bonding character. The fact that boron chains appear in three different types of metal lattices is itself a support for the existence of real bonds within the chains. If the axes of the orthorhombic unit cells of the isomorphous borides TaB and CrB are compared, the ratios a_{Ta}/a_{Cr} and b_{Ta}/b_{Cr} are 1.103, whereas the ratio c_{Ta}/c_{Cr} is only 1.077. Comparing CbB and CrB the corresponding values are a_{Cb}/a_{Cr} = 1.111, b_{Cb}/b_{Cr} = 1.110, but c_{Cb}/c_{Cr} = 1.080. The lattice is thus expanding less in the direction of the *c*-axis, i.e., the direction of the boron chains, than in the other directions when going from the smaller chromium to the larger tantalum and columbium atoms. In an analogous way the existence of boron-boron bonds within the double chains and the nets may be shown, if isomorphous borides of metals with different atomic radii are compared. For the three-dimensional boron frameworks, the boron-metal distance is increased compared with the normal radius sum. This is an indication of a rigid boron framework.

Analogies between Borides and Hydrides, Carbides and Nitrides

Hydrides, borides, carbides, and nitrides of the transition elements form a group of phases with characteristic properties, as was pointed out by Hägg (18, 19). These compounds have metallic properties. If the ratio of the radius of the nonmetal (r_X) to the radius of the metal (r_{Me}) is less than 0.59, the small nonmetallic element is accomodated in a suitably sized hole in a metal lattice belonging to one of the three simple types or to the closely related simple hexagonal type. If r_X/r_{Me} is greater than 0.59, the structures are more complicated. The present investigations have shown that as long as boron appears isolated in the metal lattice, the borides are analogous to hydrides, carbides, and nitrides. Solid solubility of boron in the expanded lattices of the pure metals has been observed for thorium, zirconium, titanium, and tantalum, all giving ratios less than or near to the critical limit. For the other metals, all giving radius ratios greater than 0.59, no solid solubility seems to exist. The systems with tantalum, columbium, and titanium, with a ratio very near the critical limit, all seem to have an intermediate position between simple and complicated systems. Simple phases exist at higher temperatures, but are transformed to more complicated phases at room temperature.

For borides in which the boron atoms form boron-boron bonds, however, the limit 0.59 seems to be of less importance, as has already been pointed out elsewhere (11). Simple hexagonal metal lattices are thus observed in the borides of the AlB_2-type for radius ratios between 0.54 and 0.69. The dominating factor seems to be the hexagonal boron nets, which easily fit into a simple hexagonal metal lattice. A possible explanation might be that the boron atoms are deformed and no longer spherical when forming the strong boron-boron bonds within the nets. It might thus no longer be correct to give the value 0.86 Å as the radius of the boron atom.

The stability of the hydrides, carbides, and nitrides decreases with increasing atomic number of the transition elements within a period. Data on the stability of the borides have not been obtained, and many of them are apparently inert and stable at higher temperatures. A comparison of the boron contents of the phases richest in boron of the elements of a period shows, however, that the same tendency also seems to exist for the borides. This is most obvious in the first transition period where the phases richest in boron have a boron content (in atomic %) of at least 67 for titanium and vanadium, 67 for chromium, 57 for manganese, 50 for iron, cobalt, and probably nickel. Attempts to prepare borides of copper have been unsuccessful.

Finally it has been confirmed that the borides have metallic properties in analogy with the other members of this group.

Application of Pauling's Theory

A general theory for the metallic state has been given by Pauling (20–22). The present author has tried to use this theory for the borides, but without success. If, for instance, the bond number for the metal-boron bond is calculated for the isomorphous Me_2B-borides of the $CuAl_2$-type, the following values are obtained: 0.28 for tantalum, 0.34 for molybdenum and tungsten, 0.42 for manganese, 0.44 for iron, and 0.49 for cobalt and nickel. This increase in bond number may be an indication of an increasing strength of the metal-boron bond, but it may also merely be a consequence of the method of calculation. As all these compounds are isomorphous and thus probably energetically similar, it seems rather incredible that such a great variation in bond number for the same metal-boron bond exists. According to a rule given in (22), the bond numbers should have a great tendency to form small integral ratios, e.g., 1/2, 1/3, 2/3, 1/4, etc. No such tendency is found for the bond numbers discussed; they increase continuously when going from tantalum to cobalt.

Pauling has also used the theory on FeB (22), for which he assumes that electrons are transferred from the iron lattice to the boron to a maximum extent of about one electron per metal atom. The present author has studied all the borides with chain structures in an analogous way. Also, for these borides there is a disagreement between isomorphous compounds, and the results can only be interpreted if one assumes that electrons are transferred from the metal lattice to the boron chains. Such an electron transfer is rather difficult to correlate with the properties of the borides with chain structures. All of them are metallic and may be regarded as expanded metal lattices with boron chains in the interstices. According to the present author's opinion, it seems more probable that electrons are transferred from the boron chains to the metal lattice, contrary to Pauling's calculations. These additional electrons of the metal lattice compensate for the loss in "metallic" properties, which would result from the increased metal-metal distance.

The formation of boron chains with covalent boron-boron bonds and an angle between two adjacent bonds of roughly about 120° is also difficult to explain if electrons were transferred to the chains from the surrounding metal lattice. The electron configuration of a boron atom is $1s^2 2s^2 2p^1$, thus with three electrons in the second quantum level. If electrons are transferred to the boron chains, which appears likely according to Pauling, each boron atom would have between three and four electrons available for bond formation. With nearly four electrons per atom, however, a tendency for boron-boron double bonds would probably be visible. Neither the boron-boron distance observed nor the angle of about 120° between the bonds formed are compatible with this view. A double bond is considerably shorter than the distances observed, and the angle between two boron bonds formed by the same boron ion probably would be 180° by analogy with carbon. On the contrary, a loss of electrons is more in accordance with the existence of covalent bonds within the chains. If, in the ideal case, one electron per boron atom is lost to the metal lattice, two electrons in the second quantum level would be left, which is exactly the number necessary for each boron to form two covalent single bonds. It thus is more probable that a chain of the kind existing would be stabilized by a loss of electrons from the boron than by a transfer of electrons to the boron.

An electron transfer in the direction mentioned is also in accordance with a theory on the electron distribution in metal lattices, recently put forth by Engel (23), and accounts for the similarity between the borides with chains and Cr_3C_2, the only carbide with carbon chains, which is hitherto known. The experimental evidence thus indicates, according to the present author's opinion, that in the borides with boron chains there is an electron transfer from the chains to the metal lattice, contrary to Pauling's theory. There is a possibility that these borides are to be regarded as chain analogs of the true interstitial compounds with isolated interstitial atoms, where an electron transfer in the direction mentioned has in some instances been suggested, e.g., hydrogen in metal hydride lattices, the ϵ-and ζ-carbonitrides of iron (24). It is, of course, not the author's intention to criticize the entire metal theory of Pauling, but it seems impossible to use Pauling's calculations on many classes of interstitial structures without any modification.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the JOURNAL.

REFERENCES

1. R. KIESSLING, *Acta Chem. Scand.*, **4**, 209 (1950).
2. R. KIESSLING, ibid. **4**, 146 (1950).
3. G. HÄGG, *Z. physik. Chem.*, **B11**, 152 (1930); **B12**, 413 (1931).
4. T. BJURSTRÖM, *Arkiv. Kemi Mineral Geol.*, **A11**, No. 5 (1933).
5. R. KIESSLING, *Acta Chem. Scand.*, **1**, 893 (1947).
6. R. KIESSLING, ibid., **3**, 603 (1949).
7. R. KIESSLING, ibid., **3**, 595 (1949).
8. L.-H. ANDERSSON AND R. KIESSLING, *Acta chem. Scand.*, **4**, 160 (1950).

9. W. Hofmann and W. Jäniche, *Z. physik. Chem.* **B31,** 214 (1936).
10. P. Ehrlich, *Z. anorg. Chem.*, **259,** 1 (1949).
11. J. T. Norton, H. Blumenthal and S. J. Sindeband, *J. Metals*, **1,** 749 (1949).
12. R. Kiessling, *Acta Chem. Scand.*, **3,** 90 (1949).
13. G. Allard, *Bull. soc. chim. France*, **51** [4], 1213 (1932).
14. U. v. Stackelberg and F. Neumann, *Z. physik. Chem.*, **B19,** 314 (1932).
15. F. Laves, *Z. physik. Chem.*, **22,** 114 (1933).
16. L. Pauling and S. Weinbaum, *Z. Krist.*, **87,** 181 (1934).
17. F. Bertaut and P. Blum, *Compt. rend.*, **229,** 666 (1949).
18. G. Hägg, *Z. physik. Chem.*, **B6,** 221 (1929).
19. G. Hägg, ibid., **12,** 33 (1931).
20. L. Pauling, *Phys. Rev.*, **54,** 899 (1938).
21. L. Pauling, *J. Am. Chem. Soc.*, **69,** 542 (1947).
22. L. Pauling, *Proc. Roy. Soc.* (*London*). **A196,** 343 (1949).
23. N. Engel, *Kemisk*, **30,** 53 (1949).
24. K. Jack, *Proc. Roy. Soc.* (*London*), **A195,** 41 (1948).